Courtesy Standard Oil Co. (N.J.)

FRONTISPIECE. Workmen loading refined wax on a refrigerated box car for shipment.

The CHEMISTRY *and* TECHNOLOGY *of* WAXES

by

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To

Josephine Mary Warth

George, Henry, Philip, and Albin

Foreword

The author's chief purpose in preparing this book has been to provide a ready reference work for chemists and industrialists who require a knowledge of waxes in their line of endeavor, and for those students and technicians who may wish to extend their background in a field with which they are not familiar.

The literature on the subject of waxes is abundant, but widely scattered. A number of textbooks on the general subject of oils, fats, and waxes do exist; these, however, devote but few pages to waxes. The need for an authoritative book on the subject of waxes, alone, is at once apparent. The author has endeavored in this volume to bring together and correlate much material that is not available to one lacking the facilities of an extensive library.

The traditional organic chemistry textbooks fail to include data concerning hydrocarbons, alcohols, acids, esters, etc., of higher carbon content than those found in the fats and oils. Such high-carbon compounds are normally found as components in waxes, both natural and synthetic. Hence, the author has considered it essential to describe these compounds in detail in an extended section dealing with the chemistry of waxes. Although tabular information on such items as the hydroxy and dibasic acids may appear overdrawn, it should prove useful to the investigator delving into the chemistry of wax metabolism in the growth of plants—a subject about which little is known.

The chemical constitution of many of the plant waxes, even of the well known ones, is not yet fully understood, but considerable progress has been made in that direction in the last decade. The results of research in this field have been assembled here. Adequate space has also been devoted to a survey of the petroleum waxes—a study of growing importance since the introduction of the comparatively new *petroleum ceresin* or *microcrystalline waxes* on the market.

The industrial application of waxes is a subject deserving wide attention. The need for a text which would not only cover the chemistry and description of waxes, but also their use in the arts and industries, was first brought to the author's attention by Carl Dame Clarke, of the University of Maryland School of Medicine, who encouraged him to undertake the task of writing this book. Similar encouragement has been given by others associated with the refining of waxes from petroleum.

Detailed acknowledgment of all sources of information drawn upon in the compilation of the data herein presented would not be possible within the brief space afforded, but an effort has been made to acknowledge the efforts of coworkers in the references cited at the end of each chapter. In particular, the author wishes to acknowledge the aid and encouragement given him by members of the American International Academy. Thanks are also due Miss Jill M. Sternberg of the Reinhold Publishing Corporation for her cooperation in the preparation of this volume.

ALBIN H. WARTH

Baltimore, Maryland
April, 1947

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Chapter 1

Introductory

Perhaps civilized man would never have developed at all, were it not for the fact that he was confronted at the very beginning with things in nature which he could not possibly pass by. He then learned to utilize these phenomena to his own advantage, and later to search for others that were useful for his welfare. Today man has advanced to the stage of development where he is learning to combine the elements in the soil, the water, and the air to synthesize natural products, and is taking care of his future needs.

So it is with wax. Wax is as old as man. The English term *wax* is derived from the Anglo-Saxon *weax*, which was the name applied to the natural material of the honeycomb of the bee. When a material of similar resemblance was found in plants it also became known as *weax* or *wachs*, and later *wax*. In modern times the term *wax* has taken on a broader significance, and is generally applied to all wax-like solids and liquids found in nature, and to those that occur individually in waxes, such as the hydrocarbons, acids, alcohols, and esters, irrespective of their source or method of preparation. Certain synthetic compounds which are not waxes from the standpoint of chemical composition, but do have waxy physical characteristics, are included because of their value in technical use as wax substitutes.

Many plants produce wax in small quantities in their tissues, in their pollen, and in their seeds, but it chiefly appears abundant as an excretion upon their leaves, stems, or fruit. In some instances this secretion is abundant and is of great importance to the plant; in desert plants it provides a surface coating which retards evaporation. A few plants produce wax in sufficient amount to be of economic importance. Such is the carnauba palm, of the dry arid regions of northeastern Brazil, the leaves of which are cut, dried, and beaten to detach the wax. The candelilla plant from the desert regions of Mexico furnishes a wax which is obtained by boiling its stems and leaves. Bayberry shrubs on the sand dunes of the Atlantic coast yield a wax when their berries are boiled.

When the term *wax* is used without further designation it has been customary to cling to the old definition, namely, that produced by the domesticated bee. Formulas still call for yellow wax or white wax, which are to be interpreted as *yellow beeswax* and bleached *white beeswax*. In fact, both the United States and British pharmacopœias cling to this definition, classifying these waxes as *cera flava* and *cera alba* respectively. Paraffin wax is simply "paraffin" or in Latin *paraffinum* (very little affinity); and natural earth wax is referred to as "ceresin," derived from *cera* and *sine*, meaning *without wax*, or a genuine, flawless article (from the custom of concealing defects in pottery and ceramic ware by patching them with wax).

When we speak of wax figures, it brings to mind the fact that since earliest times these have been made of beeswax. *Beeswax* has properties which allow it to be cut and shaped with facility; it melts to a limpid fluid at a low heat; it mixes with any coloring matter and takes surface tints well; and its texture and consistency may be modified by earthy matters and oils or fats. It is these properties which make it a most convenient medium for preparing figures and models, either by modelling or casting in molds. It was so used by the ancient Egyptians, by the Greeks, and then the Romans, and later in the Renaissance in Italy. In Spain beautiful wax figures of saints, distinguished in form and coloring, were achieved in the realm of religious art. The use of beeswax in medical art was first practiced in Florence, and is now very common. The most famous exhibition of waxworks was that of Marie Tussaud in London.

Plant and animal waxes are, generally speaking, compositions made up largely of non-glyceryl esters formed in nature by the union of higher alcohols with the higher fat acids, and with which are associated one or more of the following components: free fat and wax acids, free monohydric alcohols and sterols, hydrocarbons, and lactones or other condensation compounds. The components vary greatly in amount in accordance with the source from which the wax has been derived. Mineral wax, when derived by direct extraction from ligneous coals, contains wax esters, free wax acids, alcohols, and ketones. If obtained by destructive distillation in nature, or in the refinery, the waxes contain only hydrocarbons, which are termed the end products.

Compounds that can be isolated or artificially produced from waxes are classed as waxes, *e.g.*, the ester *cetyl palmitate* produced from *spermaceti*; or *cetyl alcohol*, produced artificially by the hydrolysis of spermaceti.

In modern wax technology it would seem highly desirable to include in our broad definition of wax, all the wax-like substances irrespective of source, since in the art of production or reproduction we aim to have before us the whole field of wax or wax-like substances from which we can select those which may best suit our needs. Waxes are used in the arts because of their peculiar physical characteristics, and seldom because of their chemical nature.

In this volume an attempt is made to bring to the reader a more thorough understanding of the chemistry of waxes, and much new informative material that will not only be of academic interest, but may well lay the ground for considerable research in a field that will become one of still greater economic importance than it is today.

Chapter 2

Chemical Components of Waxes

Formation of Waxes by Metabolism

The process of building the chemical composition of a plant begins in the chloroplastid of the cell structure. Whether this metamorphosis occurs only in connection with the living cell is a question still unanswered. According to Stobbe[17], the chlorophyll of the plant exhibits selective absorption of the less refrangible spectrum energy, and may act either directly on the H_2O and CO_2 or as a catalyst in photosynthesis, like the optical sensitizers of orthochromatic photography.

In the photosynthetic processes of plants we have:

$$CO_2 + H_2O \rightarrow O_2 + {>}CHOH$$

The CHOH grouping known as hydroxymethylene is a tautomer of CH_2O. It is incapable of existing free, except in a nascent state, and five or six of these CHOH groups would unite to give a compound of the type of inositol, $C_6H_6(OH)_6$, which is very widely diffused in nature. If one of the H atoms of the OH groups is transposed to the adjoining C, an aldose sugar, $HOCH_2[CH(OH)]_4\,CHO$ is formed.

Just as the effect of light is to do work of a chemical nature in the formation of a substance, chemical decompositions can be brought about without the aid of light by unorganized ferments or enzymes, many of which act as catalysts in processes of hydrolysis, for example: lipases hydrolyze glycerides, and sterases hydrolyze esters; oxidases bring about oxidation; reductases reduce aldoses or aldehydes to alcohols; and carboxylases eliminate CO_2 from acids. The enzymes are unstable nitrogenous compounds of colloidal nature, but not necessarily proteins.

According to their origin in a plant, the cellulose walls may be divided into groups: (1) lignocellulose walls; (2) protective cellulose walls; (3) mucilage cellulose walls; (4) reserve cellulose walls, and (5) mineral cellulose walls. It is the protective cellulose walls that are composed of mixtures of lignocellulose, oils and waxes, and frequently contain in addition resins or other substances. Just as a starch grain may attain such size as to burst through the boundary wall of the plastid to form reserve starch, the wax may exude from its border cell to form rods or granules.

The chemistry of plant metabolism seems to be more or less of the following order. The alcohols in the growing plant assimilate carbon dioxide, with the aid of activating nitrogen, to form hydroxy acids, one step higher in the number of carbon atoms:

$$\underset{\text{(even C)}}{ROH} + CO_2 \rightarrow \underset{\text{(odd C)}}{ROCO_2H}$$

The hydroxy acids unite with hydrocarbons having an odd number of C atoms. We denote these as R'H. The reaction between the hydrocarbons and hydroxy acids forms esters, *i.e.*, mixed esters and water.

$$\underset{\text{(odd C)}}{R'H} + \underset{\text{(odd C)}}{HOCO_2R} \rightarrow \underset{\text{(even C)}}{R'CO_2R} + H_2O$$

Decarboxylation of the esters takes place to yield hydrocarbons, the latter always with an odd number of C atoms. Hence, residues of hydrocarbons, called end-residues, have an odd number of carbons:

$$\underset{\text{(odd C)(odd C)}}{R'CO_2R} \rightarrow \underset{\text{(odd C)}}{R'R} + CO_2$$

This particular decarboxylation is common to arid plants, and is also produced by insects of the wax-producing type.

Plant alcohols and aldehydes usually have an even number of C atoms and through oxidation form acids with the same number of carbons:

$$\underset{\text{(even C)}}{R'\cdot CH_2OH} + O_2 \rightarrow \underset{\text{(even C)}}{R'\cdot CO_2H} + H_2O$$

$$\underset{\text{(even C)}}{R'\cdot CHO} + O \rightarrow \underset{\text{(even C)}}{R'\cdot CO_2H}$$

The alcohols and acids unite, with the elimination of a mole of water, to form ester end products.

$$\underset{\text{(even C)}}{R'\cdot CH_2OH} + \underset{\text{(even C)}}{R'\cdot CO_2H} \rightarrow \underset{\text{(even C)}}{R'\cdot CO_2R} + H_2O$$

(Also see metabolism of wax components in arid plants, p. 4)

Chemical Compounds in Waxes

In elucidating the chemistry of the components of the animal and vegetable waxes, reference will be made first to the higher aliphatic hydrocarbons, the foundation stones upon which the chemical structure of the wax alcohols, wax acids, and wax alkyl esters is built. The same hydrocarbons are the principal constituents of the paraffin waxes.

Listings of the lower hydrocarbons and their derivatives will be omitted, first, because they are not constituents of waxes, and secondly, because information concerning them is readily to be found in any elementary textbook on organic chemistry. It is difficult to secure, even from the more advanced texts on organic chemistry, ample information concerning the aliphatic compounds with a very large number of carbon atoms; yet it is these compounds that are the principal or most important constituents of waxes. It is for this reason that the wax hydrocarbons, alcohols, acids, and esters will be listed and described, together with pertinent matter on the sterols, lactones, and ketones, and some of their physical constants.

Hydrocarbons. The hydrocarbons of particular interest in waxes are those saturated hydrocarbons of the fatty acid series that range from about 14 to 44 carbon atoms. The same is true of the corresponding straight-chain alcohols and fatty acids, the esters being combined from these same alcohols and acids. The chemical relation between these compounds is simple:

$R{-}CH_2{\cdot}CH_3$	$R{-}CH_2{\cdot}CH_2OH$	$R{-}CH_2{\cdot}COOH$	$R{-}CH_2{\cdot}COOR'$
hydrocarbon	*alcohol*	*acid*	*ester*

Grouping the carbon, hydrogen, and oxygen atoms we can write the relation, where *n* denotes the number of carbons, thus:

CH_{2n+2}	$C_nH_{2n+2}O$ or $C_nH_{2n+1}OH$	$C_nH_{2n}O_2$	$C_nH_{2n-1}OOR'$ or $C_{2n}H_{4n}O_2$
hydrocarbon	*alcohol*	*acid*	*ester*

Hydrocarbons appear as important constituents of many animal and vegetable waxes, and are the sole constituents of the petroleum waxes. Marine liquid waxes contain unsaturated hydrocarbons which as a rule have far lower melting points than the saturated hydrocarbons. The melting point of a hydrocarbon increases in a regular manner with the number of carbon atoms it contains, and thus affords considerable assistance in identifying the hydrocarbon when isolated from the wax.

Alcohols. The wax esters as a rule are difficult to saponify, and the straight-chain alcohols and sterols hydrolyzed therefrom, because of their insolubility in cold alcohol and water, are found together with the hydrocarbons in the unsaponifiable portion or residue of the wax after saponification.

The important higher aliphatic alcohols, free or combined, are *monohydric* as far as waxes are concerned; the dihydric and trihydric alcohols belong mostly to the vegetable and animal oils. *Glycols* are dihydric alcohols, and *glycerols* are trihydric. There exist a few natural unsaturated higher aliphatic alcohols in the marine liquid waxes, and these will be referred to later. *Sterols* appear in the unsaponifiable residues of a few waxes, especially those which approach fats or oils in their composition. The sterols are unsaturated cyclic alcohols having a phenanthrene skeletal base. *Ketonic alcohols* are encountered rarely, and *ketones* and *lactones* only occasionally as components in the natural waxes.

Acids. The higher fatty acids, both free and combined, are important constituents of solid waxes of both animal and vegetable origin. The unsaturated acids play an important role in the liquid waxes. *Dibasic acids* are found in a few of the waxes, and are associated with the glyceryl radical as partial components. *Hydroxy acids* play a definite role in plant metabolism, and are often found as constituents of waxes; *lactones* are often found with them.

Esters. Esters, also referred to as acid esters, are the more important constituents of substantially all of the natural waxes. They are products of metamorphosis in which the alcohols and acids unite with the elimination of a mole of water. The melting point of an ester is somewhat higher than that of the corresponding acid, and is somewhat influenced by the melting point of the alcohol to which the ester acid has been linked. All known esters in waxes have an even number of carbon atoms: Less than fifty esters have been positively identified as wax components. Some of the esters are hydroxy acid esters. (See wax esters, p. 31).

Wax Hydrocarbons

Saturated Hydrocarbons. The following is a list of the straight-chain saturated hydrocarbons which have a melting point higher than 0°. These hydrocarbons are associated with liquid and solid waxes.

The hydrocarbons associated with waxes are not necessarily straight-chain, as some have one or two side chain linkings. For example *cerane,* from *iso-ceryl alcohol,* is a forked-chain hydrocarbon. It melts at 61°, and boils at 207° under 0.7 mm pressure; *melissane* from melissyl alcohol is *iso-hentriacontane,* m. 73–74°, b. 222° under 0.3 mm pressure.

There exist isomers of the normal hydrocarbons in the petroleum paraffins, although they are difficult to isolate for identification. In general the forked-chain isomers are of lower melting point than the normal chain. An exception is found in the isomers of *n*-hexacosane (m. 57°), since one isomer, *2-methyl pentacosane* (cerane), melts at 61°, and another isomer, *13-methyl pentacosane* at 29°. An iso-octacosane (m. 70°) has been isolated from the herb *Alchemilla alpina,* L.

Unsaturated Hydrocarbons. Unsaturated hydrocarbons are infrequently found in the natural waxes. They originate in the pyrolysis (heat melting distillation) of certain waxes, more particularly the wax ester constituents; for example, *melene* ($C_{30}H_{60}$, m. 62°) is obtainable by the distillation of beeswax, and *cerotene* ($C_{27}H_{54}$, m. 58°) from Chinese insect wax. A hydrocarbon ($C_{26}H_{52}$, m. 56.6°) has been reported as a constituent

Table 1. Saturated Hydrocarbons

Hydrocarbon	C_nH_{2n+2}	Melting Point (760 mm) (°C)	Boiling Point		Sp. Gr. at M.P. 15 mm
			760 mm (°C)	15 mm (°C)	
Tetradecane	$C_{14}H_{30}$	5.5	252.5	129.5	0.765
Pentadecane	$C_{15}H_{32}$	10.0	270.6	144.0	0.769
Hexadecane (cetane)	$C_{16}H_{34}$	18.1	286.5	157.0	0.775
Heptadecane	$C_{17}H_{36}$	22.5	295.5	170.0	0.778
Octadecane	$C_{18}H_{38}$	28.0[4a]	301.0	181.5	0.777
Nonadecane	$C_{19}H_{40}$	32.0	305.0	193.0	0.777
Eicosane	$C_{20}H_{42}$	36.7	309.7	205.0	0.7775*
Heneicosane	$C_{21}H_{44}$	40.4	313.4	215.5	0.7778
Docosane	$C_{22}H_{46}$	44.4	317.4	224.5	0.7776
Tricosane	$C_{23}H_{48}$	47.3	320.7	234.0	0.7779
Tetracosane	$C_{24}H_{50}$	51.1	324.3	243.0	0.7781
Pentacosane	$C_{25}H_{52}$	54.0	327.4†	254.0	0.7785*
Hexacosane	$C_{26}H_{54}$	56.9	330.3†	262.0	0.7787
Heptacosane	$C_{27}H_{56}$	59.5[4a]	332.5	275.0	0.7789
Octacosane	$C_{28}H_{58}$	62.0	335.7†	286.0	0.7792
Nonacosane	$C_{29}H_{60}$	64.0	338.1†	295.0	0.7707
Triacontane	$C_{30}H_{62}$	66.0	—	304.0	0.7707
Hentriacontane	$C_{31}H_{64}$	68.1	341.1	310.0	0.7799
Dotriacontane	$C_{32}H_{66}$	70.0	343.5	319.0	0.7798
Tritriacontane	$C_{33}H_{68}$	71.8	—	328.0	0.7801
Tetratriacontane	$C_{34}H_{70}$	72.9	—	336 215 (0 mm)	0.7806*
Pentatriacontane	$C_{35}H_{72}$	74.7	—	334 222 (0 mm)	0.7813
Hexatriacontane	$C_{36}H_{74}$	76.5	—	265 (1 mm) 230 (0 mm)	0.7819
Tetracontane	$C_{40}H_{82}$	81.0	—	241 (1 mm)	0.7830
Dotetracontane	$C_{42}H_{86}$	84.9	—	236 (1 mm)	
Tetratetracontane	$C_{44}H_{90}$	85.5			
Pentacontane	$C_{50}H_{102}$	92.1			
Tetrapentacontane	$C_{54}H_{110}$	95.0[4a]			
Hexacontane	$C_{60}H_{122}$	98.9			
Dohexacontane	$C_{62}H_{126}$	101.0			
Tetrahexacontane	$C_{64}H_{130}$	102.0[4a]			
Hexahexacontane	$C_{66}H_{134}$	103.6	*(crystal spacing 87.84 Å. U.)*		
Heptahexacontane	$C_{67}H_{136}$	104.1			
Heptacontane	$C_{70}H_{142}$	105.2			

*Krafft's synthetic hydrocarbons.

†Computed by Formula $\Delta n = \frac{85 - 0.01882(n-1)_2}{n-1}$

in the shell of a coccid, *Pulvinaria horii*, by Kono[7]; also in the vacuum distillation of lignite, and of Galician petroleum.

From the highest wax alcohol (m. 87–88°) of carnauba wax, Pummerer and Kranz[15] prepared a palmitate. By refluxing under 13 mm pressure of CO_2 and fractionating *in vacuo*, they obtained 70 to 80 per cent of a crude unsaturated hydrocarbon, which, when freed from palmitic acid and distilled from KOH, gave an olefin that crystallized from acetone in silver-felted crystals and had the following constants: melting point 64°, boiling point 295° at 15 mm; molecular weight in camphor 444.8, in naphthalene 466.5–492.5. The molecular weight in camphor indicates that the hydrocarbon is *dotriacontene,* and not hentriacontene as first believed. (Hentriacontene has an m. wt. of 434.80.)

In the petroleum paraffin waxes olefins are seldom encountered. Olefins of high molecular weight are not common. Hydrocarbons of the general formula C_nH_{2n}, which are found chiefly in Galician and Russian petroleums, are cyclic, of the polymethylene type and are commonly known as naphthenes. For example, cyclohexane (m. 42°) and cyclotriacontane ($C_{30}H_{60}$, m. 58°) are naphthenes. The melting points of the naphthenes are somewhat lower than those of the corresponding unsaturated normal chain hydrocarbons with the same number of carbon atoms.

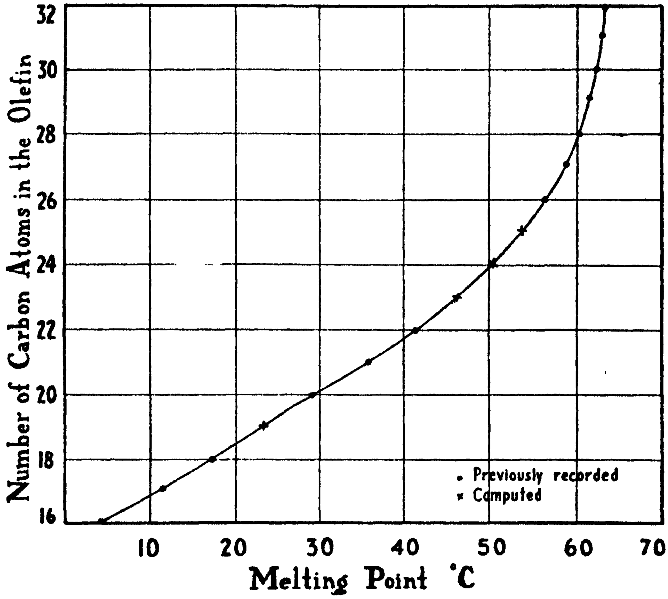


FIGURE 1. Melting points of olefins.

Olefins of the straight-chain type occurring in natural and mineral waxes are listed in Table 2. The solid series starts with *n-octadecylene* ($C_{18}H_{36}$, m. 18°, b. 179°/15 mm). This hydrocarbon is found in shark-liver oil accompanied by *squalene,* a highly unsaturated hydrocarbon. Squalene is 2,6,10,15,19,23-hexamethyltetracosahexaene-2,6,10,14,18,22.

Wax Alcohols

The unsaponifiable matter in waxes includes all those substances which remain insoluble in water after the wax has been totally saponified by adequate treatment with caustic alkali in a suitable solvent, followed by the addition of an excess of water, and the separation of the unsaponifiable by a selective solvent. In general the unsaponifiable consists of hydrocarbons and wax alcohols. Analytically, the wax alcohols are destroyed by treatment with fuming hydrochloric acid, leaving the hydrocarbons intact. Many of the ordinary animal and vegetable waxes yield 50 to 55 per cent of wax alcohols, free and combined (as esters), whereas the fats yield only 1 to 2 per cent of fatty alcohols, since the glycerin (alcohol) produced by the hydrolysis of fats is water-soluble.

Table 2. Straight-Chain Wax Olefins

Name of Olefin	C_nH_{2n}	Melting Point (°C)	Boiling Point 15 mm (°C)	Boiling Point 1.5 mm (°C)
Cetene (1-hexadecene)	$C_{16}H_{32}$	4.0 (Messer)	155	120
1-Heptadecene	$C_{17}H_{34}$	11.0 (Schmidt)	169	127
Octadecylene (1-octadecene)	$C_{18}H_{36}$	17.5 (Niemann)[14]	179	136
1-Nonadecene	$C_{19}H_{38}$	24.0*	187	144
Eicosylene (1-eicosene)	$C_{20}H_{40}$	28.5 (Niemann)[14]	196	151
1-Heneicosene	$C_{21}H_{42}$	35.5 (Schmidt)	205	158
Docosylene (1-docosene)	$C_{22}H_{44}$	41.0 (Braun)	214	166
1-Tricosene	$C_{23}H_{46}$	46.0*	223	174
Tetracosylene (1-tetracosene)	$C_{24}H_{48}$	50.0*	233	181
1-Pentacosene	$C_{25}H_{50}$	53.5*	242	188
Hexacosylene (1-hexacosene)	$C_{26}H_{52}$	56.5 (Karrer)	251†	196†
Cerotene (1-heptacosene)	$C_{27}H_{54}$	58.5	260†	203†
Octacosylene (1-octacosene)	$C_{28}H_{56}$	60.0	269†	210†
1-Nonacosene	$C_{29}H_{58}$	61.0	277†	218†
Melene (1-triacontene)	$C_{30}H_{60}$	62.0 (Brodie)	285	225
1-Hentriacontene	$C_{31}H_{62}$	63.0	291†	231†
1-Dotriacontene	$C_{32}H_{64}$	64.0	295	238†(P&K)

* Computed melting point. † Computed boiling point.

In listing the fat and wax alcohols the common nomenclature is used as in Table 3, although the Geneva is also referred to. Under the rules of the International Union set up at the Geneva Conference the final *e* of the name of a hydrocarbon becomes *'ol'* for its corresponding alcohol. For example, eicosan*e* ($C_{20}H_{42}$) and eicosan*ol* ($C_{20}H_{42}O$). If the alcohol is a normal one it can be expressed as *n-arachidyl alcohol,* or *1-eicosanol,* the latter denoting that the CH_3 group is attached to the terminal carbon, $CH_3\cdot(CH_2)_{18}\cdot CH_2\cdot OH$.

The crystal cell spacings of the alcohols differ little from those of the corresponding monobasic acids. The chain lengths increase in a regular fashion from 41.35 to 71.0 Å.U. (B. values) for the C_{18} to the C_{32} alcohol.

Melissyl alcohol (C_{31}) in beeswax is probably a mixed dimer of *myricyl* and *lacceryl alcohols. n-Montanyl alcohol* is not generally found in vegetable or animal waxes. It is a constituent of montan wax.

Table 3. Normal Saturated Monohydric Aliphatic Alcohols (C_{10} to C_{44})

Name	$C_nH_{2n+1}OH$	M.P. (°C)	B.P. (°C)	Sp. Gr. of Melt T°/4°
Capryl (decyl) (1-decanol)	$C_{10}H_{21}OH$	7.0	231/760 mm	0.8375 T = 23
Undecyl (hendecyl) (1-hendecanol)	$C_{11}H_{23}OH$	16.3[a]	243/760 mm	0.8340 T = 23
Lauryl	$C_{12}H_{25}OH$	23.8[a]	255/760 mm	0.8310 T = 24
Tridecyl	$C_{13}H_{27}OH$	30.2	155/760 mm	0.8277 T = 31
Myristyl (tetradecyl) (1-tetradecanol)	$C_{14}H_{29}OH$	37.6	165/760 mm	0.8240 T = 38
Pentadecyl	$C_{15}H_{31}OH$	43.8	176/760 mm	0.8215 T = 44
Cetyl (hexadecyl) (1-hexadecanol)	$C_{16}H_{33}OH$	49.3	187/760 mm	0.8180 T = 50
Margaryl (1-heptadecanol)	$C_{17}H_{35}OH$	54.3	——	0.8150 T = 55
Stearyl (octadecyl)	$C_{18}H_{37}OH$	58.5[b]	210/15 mm	0.8120 T = 59
Nonadecyl	$C_{19}H_{39}OH$	63.0	166/0.3 mm	0.8090 T = 63
Arachidyl (eicosyl) (1-eicosanol)	$C_{20}H_{41}OH$	66.5	176/0.3 mm	0.8060 T = 67
Heneicosyl	$C_{21}H_{43}OH$	69.5	——	——
Behenyl (docosyl) (1-docosanol)	$C_{22}H_{45}OH$	72.3	188/0.3 mm	0.8000[d] T = 73
Tricosyl	$C_{23}H_{47}OH$	74.3	196/0.3 mm	——
Lignoceryl (1-tetracosanol)	$C_{24}H_{49}OH$	76.5	210/0.4 mm	0.7950[d] T = 77
Pentacosyl	$C_{25}H_{51}OH$	79.0	215/0.36 mm	——
Hexacosyl	$C_{26}H_{53}OH$	81.0		0.7890[d] T = 81
Octacosyl	$C_{28}H_{57}OH$	84.5		0.7830[d] T = 85
n-Myricyl (1-triacontanol)	$C_{30}H_{61}OH$	87.5[c]		0.7770 T = 88
n-Lacceryl (1-dotriacontanol)	$C_{32}H_{65}OH$	89.0[b]		
Tetratriacontyl	$C_{34}H_{69}OH$	94.0		
Hexatriacontyl	$C_{36}H_{73}OH$	96.0		
Takakibyl (1-tetratetracontanol)	$C_{44}H_{89}OH$	99.0		

[a] M.p. by Verkade; [b] by Gascard; [c] by Heiduschka and Gareis; [d] computed values.

Several of the alcohols encountered in waxes are not normal, but little is known about their grouping, and they are simply referred to as isomers. *Carnaubyl alcohol,* the alcohol of wool grease, was one of the first isomers of *n*-lignoceryl alcohol to be so recognized. An *iso-ceryl alcohol* supposedly exists. Almost without exception the alcohols which are spoken of as isomers are in reality equimolecular compounds of homologs; this is particularly true of the natural alcohols with an odd number of carbons. These mixed dimers are responsible for no less than three ceryl alcohols, referred to as *neoceryl, ceryl,* and *carboceryl* ($C_{25}H_{52}O$, $C_{26}H_{54}O$, and $C_{27}H_{56}O$). These ceryl alcohols may also be referred to as (*a*), (*b*) and (*c*) respectively.

The position of monomeric alcohols in contrast with dimeric alcohols with an odd number of carbons is uncertain. As a whole, such monomeric odd carbon alcohols are non-existent. The exceptions appear to be *montanyl alcohol* in its natural state in montan wax, or in cotton, which appears to be the normal C_{29} alcohol; and *melissyl alcohol* of the waxes of arid plants, which also appears to be the normal C_{31} alcohol. These particular alcohols of very high molecular weight cannot be distinguished from synthetically prepared alcohols.

Table 4. Forked-Chain Isomers and Bimolecular Compounds of the Saturated Wax Alcohols

	Normal Alcohol	M.P. (°C)	Isomer	Mixed Dimer	M.P (°C)
		Even Number of Carbon Atoms			
C_{24}	*n*-lignoceryl	76.5	carnaubyl		69, 68[1]
	(1-tetracosanol)		isotetracosanyl		72.0
C_{26}	ceryl (1-hexacosanol)	79.8, 81.0	pseudoceryl		77.8[6]
C_{28}	1-octacosanol	83.2	koryanyl		?
			neomontanyl		82.0
C_{30}	*n*-myricyl	86.5, 88.0	gossypyl		87, 86, 82 respectively
C_{32}	*n*-lacceryl	89.0, 91.0	psyllyl		88.0
C_{34}	1-tetratriacontanol	94.0	incarnatyl		73.0
		Odd Number of Carbon Atoms			
C_{25}	1-pentacosanol	79.0	neoceryl	(C_{24}, C_{26})	75.0, 75.5[2]
C_{27}	1-heptacosanol	82.8	ceryl (c)	(C_{26}, C_{28})	79.5, 80.0[3]
			isoceryl		78.0[5]
			carboceryl	(C_{26}, C_{28})	79.0[4]
C_{29}	*n*-montanyl	84.5			
C_{31}	1-hentriacontanol	89.0	melissyl	(C_{30}, C_{32})	85.8, 87.0[2]
C_{33}	1-tritriacontanol	93.0	psyllostearyl		69.0
			ceromelissyl	(C_{32}, C_{34})	90.0
C_{35}	1-pentatriacontanol	98.0	isopentatriacontanol		89.5
			ceroplastyl	(C_{34}, C_{36})	92.0

[1] M.p. by Betrabet; [2] by Gascard; [3] by Kono; [4] by Brodie; [5] by Gottfried; [6] by Damoy.

Natural Occurrence of Wax Alcohols. Cetyl alcohol ($C_{16}H_{34}O$) occurs in the combined state as cetyl palmitate in spermaceti. Cetyl alcohol (ethal) was discovered by Chevreul over a century ago. It can now be prepared cheaply from cetyl palmitate by hydrogenation. It crystallizes from alcohol in leaflets (m. 49–50°). , *Heptadecyl alcohol* crystallizes in pearly white scales (m. 54°). *Stearyl alcohol* occurs in montan wax and in cotton, and crystallizes from alcohol in shining leaflets (m. 58.5°). *Ceryl alcohol* occurs as ceryl cerotate in Chinese insect wax, and accompanies *myricyl alcohol* in japan wax. Ceryl alcohol crystallizes in rhombic plates (m. 79.5–80°). *Myricyl alcohol* ($C_{30}H_{62}O$) and *lacceryl alcohol* ($C_{32}H_{66}O$) occur both free and combined in carnauba wax. Myricyl alcohol crystallizes from ether in needles (m. 86.5°, Robinson). *Melissyl alcohol* ($C_{31}H_{64}O$) occurs in beeswax in the combined state as *melissyl melissate.* It crystallizes in white brilliant micro-lozenges (m. 87°).

Lacceryl alcohol in the form of lacceryl laccerate (m. 94°) was discovered by Gascard[4] in the wax obtained from commercial "stick-lac." It crystallizes in brilliant pearl needles (m. 89°) consisting of lozenge-shaped micro-lamellae, characteristic of the higher alcohols of this series. An alcohol resembling laccerol has been isolated from Palaquium wax, of *P. gutta,* the gutta percha tree. *Takakibyl alcohol,* with 44 carbon atoms, is present as a wax constituent of Koryan corn oil of Manchukuo.

Some of the wax alcohols as such have been exploited commercially, *e.g., cetyl alcohol* which can be obtained directly from cetyl palmitate by hydrogenation. On the boundary line between waxes and oils is *lauryl alcohol* ($C_{12}H_{26}O$) which has long been available as an alcohol readily prepared by catalytic hydrogenation of its esters. A trade name for the commercial product is "Lorol." Lorol forms a soap with sodium which can be used in somewhat acid solutions that would precipitate the fatty acids from ordinary soaps, and a soap which can be used in salt and hard water as well.

Heiduschka and Garcis[5] determined the melting point of carefully purified *myricyl alcohol* to be 87.5°; it appears to be identical with the synthetic 1-triacontanol. The next higher homolog is *1-hentriacontanol* which has a melting point of 89.0°. They were unable to obtain a melting point higher than 85.8° for the C_{31} alcohol, *melissyl alcohol,* isolated from beeswax, despite the fact that it was believed to be identical with 1-hentriacontanol. Therefore it would appear obvious that the melissyl alcohol of beeswax is a mixed dimer or bimolecular compound of C_{30} and C_{32} alcohols.

Isomers of the normal alcohols appear to be more prevalent with those of an even number of carbon atoms. A few of the saturated alcohols with an even number of carbons have melting points far below those of the corresponding *n*-alcohols, and are undoubtedly true isomers, *e.g., carnaubyl* and *incarnatyl.* There appear to be at least three ceryl alcohols, the C_{25}, C_{26}, and C_{27}, which hereafter will be referred to as (*a*), (*b*), and (*c*) respectively. These three ceryl alcohols correspond to the known cerotic acids. Lewkowitsch[10] has referred to the C_{26} alcohol as *ceryl alcohol,* and to the C_{27} as *isoceryl alcohol.* The term *carboceryl* has been applied to the latter by other investigators, and the term *neoceryl* to the C_{25} ceryl alcohol. The C_{25} alcohol is probably a mixed dimer of lignoceryl and ceryl alcohols; the C_{27} ceryl alcohol a mixed dimer of ceryl and neomontanyl alcohol. Crystal cell spacings for melted layers of the alcohols are as follows: C_{14}, 33.0; C_{16}, 37.40; C_{18}, 41.3; C_{19}, 43.0; C_{20}, 45.3; C_{21}, 47.0; C_{22}, 50.0; C_{24}, 54.2; C_{25}, 55.5; C_{26}, 58.0; C_{28}, 62.3; C_{30}, 67.0; 6_{32}, 71.

Identification of Myricyl Alcohol of Beeswax. The attempted scheme of identification of wax components may be illustrated by a classical example of Gascard.[4a] Brodie originally had discovered what he designated as *myricyl alcohol* (m. 85°) having the formula $C_{30}H_{62}O$. Gascard attempted to show that the alcohol constituent of beeswax was not a C_{30} alcohol but an *n*-C_{31} alcohol (now known as *n*-melissyl alcohol). Gascard crystallized the alcohol from benzene and observed that it formed tiny white lozenges (m. 87°) slightly soluble in cold alcohol, ether, benzene or chloroform. He converted the alcohol to iodide (m. 69°) which gave 22.43–22.80 per cent iodine (average 22.59 per cent), corresponding to $C_{31}H_{63}I$. Sodium amalgam converted the latter to the hydrocarbon $C_{31}H_{64}$ (m. 69°) [$C_{30}H_{62}$, m. 66°; $C_{32}H_{64}$, m. 68.1° (Krafft); $C_{32}H_{66}$, m. 70.5°]. The properties of the C_{31} alcohol and its derivatives were further compared with those of the corresponding derivatives of *laccerol* (*n*-lacceryl alcohol, $C_{32}H_{66}O$), which Gascard had previously obtained from "stick-lac." By converting *melissic acid* (C_{31} acid) to the next higher homolog, he attempted to show that the *lacceric acid* so formed is identical with that which may be derived from the stick-lac wax, both melting at 95 to 96°.

	Myricyl Derivatives m.p. (°C)		Lacceryl Derivatives m.p. (°C)	
Free alcohol	87	(tiny lozenges)	89	(rhomboidal plates)
Acetate	72		73	
Iodide	69		71	(leaflets)
Corresponding hydrocarbon	69	($C_{31}H_{64}$)	70	
Dimyricyl	100.5	dilacceryl	102	
By oxidation,[a] mellisic acid	90	lacceric acid	95–96	(rhomboids)
Esters: myricyl mellisate	90.5	lacceryl laccerate	95	
		myricyl laccerate	92.5[b]	
By KCN[c]: melissyl cyanide from iodide	75	—	—	—
Cyanide on hydrolysis[d]: lacceric acid	95–96	—	—	—

[a] Oxidized with CrO_3 in acetic acid (or by heating in soda lime).

[b] Also prepared by the action of iodine on silver laccerate.

[c] With potassium cyanide in methyl alcohol at 150° in bomb tube.

[d] Hydrolyzed by heating at 170° in amyl alcohol.

NOTE: In view of our more recent knowledge, *n*-melissic acid when synthesized has a melting point of 92.8°. (The copolymer C_{30}, C_{32} has an m.p. of 90°). The copolymer on reduction yields the C_{31} hydrocarbon. *Melissyl melissate* (C_{31}, C_{31}) when synthesized has a melting point of 92.5°. The m.p. given by Gascard would correspond to a mixture of the monomeric C_{30}, C_{30} and C_{32}, C_{32} esters, which are practically inseparable by methods used at that time. The synthetic C_{31} alcohol melts at 89°. The mixed dimeric alcohol C_{30}, C_{32} melts at 85.8°, or appreciably lower than the C_{30} alcohol, which melts at 88.0°.

Unsaturated Alcohols. Unsaturated aliphatic alcohols of the monoethylenic type are commonly associated with the liquid waxes. Most of them are liquids, but a few are solids of low melting point. The names bear the ending -eyl, -enyl, or -enol, and the hydrocarbons related thereto have the ending -ene.

Zoömaryl alcohol ($C_{16}H_{32}O$) has the constitution:

$$CH_3 \cdot CH_2 \cdot (CH_2)_3CH_2 \cdot CH : CH \cdot CH_2 \cdot (CH_2)_5 \cdot CH_2 \cdot CH_2OH$$

and is designated as *7-hexadecen-16-ol,* or *9-hexadecen-1-ol,* depending upon the terminal carbon from which the double bond is counted. Unsaturated alcohols are optically right- or left-handed, that is, *cis* or *trans*; for example, *oleyl alcohol* ($C_{18}H_{35} \cdot OH$) is *cis-9-octadecen-1-ol.* Alcohols of diolefins are also encountered in the liquid waxes; for example, linoleyl alcohol $\Delta^{9:10,\ 12:13}$, which may be written 9-12-octadecen-1-dienol.

The following is a partial list of unsaturated alcohols:

$C_{10}H_{19} \cdot OH$	Decenol, a liquid wax constituent of wool grease. Isodecenol (1-decen-10-ol) b_{13} 143–4°.
$C_{11}H_{21} \cdot OH$	Hendecenol (1-undecen-11-ol), likewise a constituent of wool grease, m. − 7°, $b_{4.5}$ 148.5°.
$C_{12}H_{23} \cdot OH$	Dodecenol, a liquid wax.
$C_{14}H_{27} \cdot OH$	Physeteryl alcohol, 6-tetradecen-14-ol; iodine no., 111.2.
$C_{15}H_{29} \cdot OH$	Pentadecenol, m. 32.5°, b_{10}, 170–2°. Isopentadecenol (1-pentadecen-13-ol) m. 40.2°, b_8 170°.
$C_{16}H_{31} \cdot OH$	Zoömaryl alcohol, iodine no. 98.6, a constituent of marine oils. Also palmitoleyl alcohol of beeswax.
$C_{18}H_{35} \cdot OH$	Octadecenol, or oleyl alcohol of marine oils. It is definitely *cis*-9-octadecenol; b_{15} 205–10°.
$C_{20}H_{43} \cdot OH$	Docosenol, a constituent of jojoba oil; closely related is the isomer, erucyl alcohol.
$C_{24}H_{47} \cdot OH$	Carnaubenol (carnaubanyl alcohol) m. 39°, a disputed constituent of carnauba wax.
$C_{26}H_{51} \cdot OH$	Hexacosenol, m. 42°, of jojoba oil.

Sterols

The sterols are polycyclic alcohols that often accompany fats and oils, and to a lesser extent waxes of both animal and vegetable origin. They are insoluble in water, and appear in the unsaponifiable residues of the waxes of which they sometimes constitute a significant proportion. In the original source the sterols may occur either in the free or the combined state, the latter as esters of the wax acids, or both. *Cholesterol* has four rings (phenanthrene skeletal base), an unsaturated bond, and an OH (alcohol) group. *Stigmasterol* has two double bonds. *Dihydrocholesterol,* derived from cholesterol, has two hydrogen atoms saturating the double bond. Other dihydrosterols may or may not have a double bond. *Dihydroxysterols* have two OH groups positioned where the unsaturated double bond would otherwise exist. The general ring structure will be referred to later.

The free sterols are characterized by their power of forming crystalline additive compounds with the glucoside principle *digitonin.* Of the animal sterols (zoösterols) the most abundantly found in nature is *cholesterol* [$C_{27}H_{45}(OH)$] which forms small needle-shaped anhydrous crystals (m. 148.5°) optically active in chloroform solution. Cholesterol has a specific gravity of 1.052 to 1.053. It sublimes at 200°, and distills unchanged *in vacuo*. It is freely soluble in hot alcohol, choloroform, ether and carbon bisulfide, and less soluble in acetone, petroleum ether, benzene, and glacial acetic acid. Cholesterol has an iodine number of 68.2.

Cholesterol is an important component of *lanolin* and is said to stimulate hair growth. Associated with cholesterol in lanolin is another sterol, 7 : 8-dihydrocholesterol [$C_{27}H_{47}(OH)$, m. 142–143°], which when subjected to ultraviolet light can be activated to a form of vitamin D (vitamin D_3). Dihydrocholesterol is dextro-rotary, $[\alpha]_D$ 28.8.

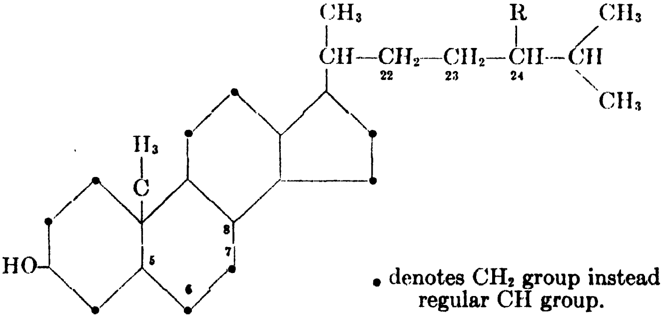
Isomeric forms of the zoösterols, such as *iso-cholesterol* (m. 140°), are dextro-rotary, whereas cholesterol is levo-rotary, $[\alpha]_D$ -38.8. The zoösterols are found in liquid marine waxes.

In the vegetable kingdom there exist the corresponding cyclic alcohols, known as *phytosterols*; of these *sitosterol* [$C_nH_{2n-9}(OH)$] is the most widely distributed. Sitosterol [$C_{29}H_{49}(OH)$] crystallizes in tufts of stumpy needles (m. 138°). It is levo-rotary $\left[\alpha\frac{30}{D} = -19.5\right]$. In 1934 Bergmann[1] was able to show that a zoösterol known as *ostreasterol*, found in mollusks, yielded upon reduction, *ostreastanol* the same as *sitostanol*, $C_{29}H_{51}(OH)$, obtained in reducing sitosterol. To quote Bergmann, "the fact that ostreastanol is identical with sitostanol must be regarded as very significant because this is the first time that a sterol obtained from animal sources has been converted into a typical sterol of plant origin. It raises the question, therefore, whether a strict line can be drawn at all between *zoösterols* and *phytosterols*." The formula of *ostreasterol* [$C_{29}H_{47}(OH)$], is isomeric with *stigmasterol*, a phytosterol found in sugar cane. *Paracholesterol* [$C_{26}H_{43}(OH)$], is found in wheat oil. It crystallizes from ether in silky needles (m. 134–134.5°). Sometimes a name is given to what seems to be a new sterol but later proves to be a complex mixture of sterols, *e.g.*, in the case of *asteriasterol* of the starfish.

Sterols with a double unsaturated group replaced by H atoms in the chemical structure, such as *β-cholestanol* ($C_{27}H_{47}(OH)$, m. 128–9°] are known as *dihydrosterols* [$C_nH_{2n-7}(OH)$]. *Clionasterol*, which is 5 : 6-dihydrostigmasterol, with but one double bond, is found in sponges. In plant life a new sterol, *arisaesterol* (m. 135°) was discovered by Marion[11] in the corms of the jack-in-the-pulpit, *Arisaema triphyllum* (L) Schott. It has the formula $C_{36}H_{62}(OH)_2$, and is a *dihydroxysterol*, of type $C_nH_{2n-10}(OH)_2$.

A sterol that is highly unsaturated is to be found in *ergosterol*, a constituent of the ergot in rye. Ergosterol has the formula $C_{28}H_{43}(OH) \cdot H_2O$, of the type $C_nH_{2n-13}(OH)$, to which *agnosterol* [$C_{30}H_{47}(OH)$] of wool fat belongs. Ergosterol crystallizes in monoclinic needles with an m.p. of 165°. Although ergosterol is a plant sterol about, 0.01 per cent has already been found in wool wax alcohols. Ergosterol differs from cholesterol in having two extra double bonds, one being in the side chain.

Sterols are derivatives of cyclopentanperhydrophenanthrene and are chemically related to the bile acids and sex hormones. The skeletal formula given below is common to all the sterols in its cyclopentenophenanthrene ring structure.



• denotes CH_2 group instead of the regular CH group.

By replacing the single bond with a double bond in ring position 5 : 6 and replacing R in position 24 with H, we would have the structural formula of cholesterol. By replacing the single bond of cholesterol with a double bond in the 7 : 8 position, and providing a double bond for the 22 : 23 position in the side chain, making 3 double bonds in all, we would have ergosterol. The substitution of a double for a single bond requires the elimination of two hydrogen atoms.

Esters of Sterols. Cholesterol forms an ester (m. 79°, after sintering) with lauric acid, an ester (m. 78°) with myristic acid, an ester (m. 77–79°) with palmitic acid, an ester (m. 82°) with stearic acid, and an ester (m. 85.5°) with cerotic acid. Cholesteryl oleate crystallizes in thin needles (m. 42°). Cholesteryl palmitate crystallizes in both plates and long needles. Cholesteryl stearate crystallizes in short needles.

Monobasic Fat and Wax Acids

Each saturated straight-chain hydrocarbon has a corresponding acid. If the carboxylic group is attached to the terminal carbon atom, the acid is referred to as a normal acid, and is simply written *n*-acid. For example, *n*-octane yields *n-caprylic acid* (n-$C_8H_{16}O_2$), which may be written $CH_3(CH_2)_6 \cdot COOH$ or $H(CH_2)_7 \cdot COOH$, or in any convenient manner to show a continuation chain of simple CH_2 linkages throughout to the terminal carbon atoms. The empirical formula for the series of acids is $C_nH_{2n}O_2$.

Although the texts often state that the monobasic acids with an even number of carbon atoms are those that are almost entirely associated with natural oils, fats and waxes, this statement is not strictly true with respect to the waxes, as recent research into their constitution shows that there are a few wax acids with an odd number of carbons.

The following is a brief description of the appearance of the solid saturated acids encountered in oils, fats and waxes.

Caprylic acid ($C_8H_{16}O_2$) crystallizes in the cold in leaflets which melt at 16.5°.

Capric acid ($C_{10}H_{20}O_2$) crystallizes in fine leaflets, and in colorless needles.

Umbellulic acid ($C_{11}H_{22}O_2$) crystallizes in leaflets.

Lauric acid ($C_{12}H_{24}O_2$) crystallizes from ethanol in needles.

Myristic acid ($C_{14}H_{28}O_2$) crystallizes in leaflets.

Palmitic acid ($C_{16}H_{32}O_2$) crystallizes from hot ethanol in fine needles and in pearly scales when absolutely pure.

Margaric acid ($C_{17}H_{34}O_2$) crystallizes from ethanol in rhombic lamellas, melts at 59.8°; daturic acid (isomer) 54.5°.

Stearic acid ($C_{18}H_{36}O_2$) crystallizes in leaflets, m. 69.3°.

Arachidic acid ($C_{20}H_{40}O_2$) crystallizes in lustrous scales, m. 76.3°.

Behenic acid ($C_{22}H_{44}O_2$) crystallizes in colorless needles, m. 80.7°.

Lignoceric acid ($C_{24}H_{48}O_2$) crystallizes in colorless needles from alcohol, and melts at 89.2°.

Cerotic acid ($C_{26}H_{52}O_2$) crystallizes in micro-needles from alcohol, and melts at 84.2°, when the acid has been synthesized.

Carboceric acid ($C_{27}H_{54}O_2$) crystallizes from ethyl acetate in needles, m. 82°.

Neomontanic acid ($C_{28}H_{56}O_2$) crystallizes in glistening scales, m. 86°.

Myricinic acid ($C_{30}H_{60}O_2$) crystallizes in silky scales.

Melissic acid ($C_{31}H_{62}O_2$) crystallizes in needles from alcohol, or rhombic plates (lozenges) from benzene.

Lacceric acid ($C_{32}H_{64}O_2$) crystallizes from benzene in lozenges.

Most of the higher saturated aliphatic acids and their derivatives when pure assume the form of lozenge-shaped, microplates whose small diagonal divides them into two equilateral triangles.

Unit Cell Crystal Structure of Wax Acids. The crystal cells of myristic, palmitic, stearic acid, etc., are monoclinic prismatic, and contain four molecules, which have been considered as hybrids of dimers, in which there are resonating hydrogen bonds. The hybrids are attached by the CO linkage of the COOH groups. The long hybrid cells are bundled, and at the end appear to have an elliptical cross-section. The length of the dimer of palmitic acid is 39.93×10^{-8} cm (39.93 Å.U.), or double that of the molecule, 19.60 Å.U.; the first measurement is from x-ray observation, and the second by surface tension measurements made by Langmuir.[8] The bond between the CH_2 groups is 1.21 Å.U. in length, and shortens slightly for higher acids in the series. The full dimensions of the crystal cell (4 molecules) of stearic acid as given by Alex Müller are $a = 5.546$, $b = 7.381$, $c = 48.84$ Å.U., $\beta = 63.38$. The latter is the angle that the c axis is inclined from the basal plane. Crystals of stearic acid represent a recrystallization of the pure acid from carbon bisulfide.

Isomers of Wax Acids. In Table 5 (p. 22) the empirical formula for the acid is given, so that each fat or wax acid may at a glance be referred back to its hydrocarbon in Table 1. The increment between the melting points is connoted by staggering the odd carbon acids from the even ones. Common or distinctive names are given when possible for the normal chain acids, and also for those forked-chain isomeric acids that occur in the natural state in waxes.

Most texts list the acids found in waxes as *n*-aliphatic fatty acids. Studies of Francis and his associates tend to show that the pure *n*-aliphatic acids, prepared synthetically, do not always correspond, in melting point or other physical properties, to similar acids with the same number of carbon atoms isolated from natural waxes. This brings up the questions whether the fat or wax acids isolated are really in the pure form, whether they are mixtures of homologs exhibiting a binary molecular form, or whether they are simply forked-chain isomers. To illustrate the point in question: texts list *cerotic acid*, a C_{26} acid, as n-$C_{26}H_{52}O_2$. The latter is *1-hexacosanic* acid with a melting point of 87.8°; its homologs, n-C_{25} and n-C_{27} acids, melt at 83.5° and 87.0° respectively. Repeated crystallizations of the cerotic acid isolated from natural waxes never yield a purified cerotic acid of as high a melting point as the *n*-acid. It is not improbable that the C_{26} cerotic acid might exhibit a bimolecular state, in which case the melting point would be abnormally low (see p. 24). Molecular weight determinations seem to substantiate this hypothesis.

The cerotic acid of scale-insect waxes is a C_{27} acid, as confirmed by many investigators; the name *cerotic* was first given to a C_{25} acid, which later became known as *hyaenic* acid (m. 77.8°). Gascard assigned the name *neocerotic* to the C_{25} cerotic, and *carbocerotic* to the C_{27} cerotic. The name *isocerotic* infrequently appears in chemical literature for the C_{27} acid.

Although molecular distillation has not substantiated the existence of anything but acids with an even number of carbon atoms in their make-up for the wax esters, there does exist substantial evidence that the free acids in the natural waxes may have an odd or even number of carbon atoms. The acids in the esters generally have an even number. The melting points of the cerotic acids range from 77.8° to 82.5° in their purified state. Cerotic acid, in its broad sense, is one of the oldest wax acids known, and yet uncertainty surrounding its constitution has not been entirely cleared (see p. 23). For convenience, the C_{25} cerotic is referred to as cerotic acid (*a*), the C_{26} cerotic as (*b*), and the C_{27} cerotic as (*c*).

Yamazaki[20] in 1941 reported a melting point of 77.5–78° for the cerotic acid obtained by the oxidation of the ceryl alcohol (*a*) (m. 75–76°) isolated from beeswax. According to Lewkowitsch,[10] pure cerotic acid crystallizes from alcohol in stellate microscopic needles, melting at 77.8°; from benzene in dense laminae; and from ether in tabular masses consisting of large aggregated needles. He states that in Riggs' opinion a cerotic acid which crystallizes in needles must still be considered as impure, the criterion of purity being crystallization in pearly scales (nacreous crystalline plates). The melting point of the strictly pure C_{26} cerotic acid is not stated, but in the light of more recent knowledge it appears to be 79° when crystallized from a non-polar solvent.

Kiesel[6], in a classical experiment in 1925, isolated a pure wax acid from the spores of *Aspidium filix-mas* and *Asplenium filix-foemina*, L., both species of ferns. The acid had a melting point of 85 to 85.5°. From beeswax after tedious recrystallizations from alcohol, then from ether, followed by preparation of the K salt and crystallization of this from alcohol, he was able to secure what he firmly believed to be *cerotic acid* with a melting point of 83 to 84°. The acid from the fern spores did not depress the melting point of the acid from beeswax and was thus proved pure.

Positioning Acids in Series by Interplanar X-ray Spacings. In plotting the melting points of the fatty acid series there are two curves which run quite parallel, one for the acids with an even number of carbons, the other for the odd. The reason for this phenomenon is apparently linked with that of the structure of the unit crystal cell of the acid. The melting point of the odd-carbon acid is close to that of its lower even-carbon homolog, and the same holds true of the crystal spacings. For example,

Acid		Melting Point (°C)	C Spacing (x-ray)d-
Palmitic	C_{16}	62.9	35.6×10^{-8} cm
Margaric	C_{17}	61.3	36.9
Stearic	C_{18}	69.9	39.7
Mixed dimer	C_{16}, C_{18}	57.9	38.8

The equimolar copolymer of palmitic and. stearic has a somewhat higher d-(long axis) spacing than n-margaric acid, but a much lower melting point.

Francis[3] attempted to show that the lignoceric acid of beechwood tar is the same as the normal synthetic lignoceric acid, n-$C_{24}H_{48}O_2$, and that the iso-lignoceric acid described by Brigl and Fuchs is in reality a mixture of homologs. Francis found the x-ray spacings of n-lignoceric acid to be 58.5 and 52.8 Å.U., both specimens melting at 83.4°. The acid from beechwood tar also melted at 83.4°, and its spacings were 58.4 and 52.7 Å.U. The iso-lignoceric acid of Brigl and Fuchs, gave two spacings (pressed on slide) 57.2 and (melted) 52.52 Å.U., and a melting point of only 74.5°. Francis concluded that the latter is a mixture of C_{23} and C_{24} acids. At the same time he stated that the spacings of an equimolar mixture of these two acids are 57.5 and 52.0 Å.U., but the melting point is 79.8°. The melting point of 74.5° could indicate that the acid of Brigl and Fuchs is a mixture of the copolymers C_{22}, C_{24} and C_{24}, C_{26}, since these acids would show a depressed melting point of that degree. On the other hand, Meyer, Brod and Soyka[12], from their extensive study of lignoceric acid obtained from peanut oil and beechwood tar, definitely conclude that natural lignoceric acid does not have a normal chain.

Any acid of the fat and wax acid series falls into one of the three following classes: (1) normal, (2) mixed dimer; and (3) isomer (CH_3 group not in the 1-position). (Tables 5 and 6). The (3) type of isomer should show a shorter axis of the unit cell and a lower melting point. It is obvious that the so-called iso-lignoceric acid would fall in class (2).

The following are the interplanar x-ray spacings of the fat and wax acids. B spacings are for crystals from a non-polar solvent, and C for the melts. Figures are in Angstrom units (Å.U.) 10^{-8} cm, for d_1 crystal spacings.

	N-Acids	B (Å.U.)	C (Å.U.)
C_{16}	palmitic	39.1	35.6
C_{17}	margaric	40.4	36.9
C_{18}	stearic	43.7	39.7 (39.9)
C_{19}	nonadecylic	---	40.8
C_{20}	arachidic	48.4	44.3
C_{2}	medullic	49.2	45.0
C_{2}	behenic	52.9	48.3
C_{2}	tricosanic	53.4	50.3
C	lignoceric	57.7	52.6
C_{2}	pentacosanic	----	53.5
C_{26}	hexacosanic	62.2	56.2 (56.6)
C_{28}	octacosanic	67.1	61.0
C_{30}	triacontanic	71.4	65.7
C_{32}	lacceric	76.3	69.2
C_{34}	tetratriacontanic	80.5	73.3
C_{36}	hexatriacontanic	85.2	78.1
C_{38}	octatriacontanic	90.0	82.1
C_{46}	hexatetracontanic	108.2	99.0
C_{16}, C_{18}	bimolecular compound	----	38.85*

* (Francis, Collins, and Piper)

Crystals of acids containing an even number of carbon atoms obtained by deposition from such non-polar solvents as dimethyl ketone or benzene show the B crystal spacings, whereas from ethanol they give the C spacing only; acids containing an odd number of carbon atoms show the B spacings irrespective of the solvent used in their preparation.

The Fat and Wax Acids and Their Natural Occurrence. The acids of the n-$C_nH_{2n}O_2$ series, with the lower number of carbon atoms, not given in Table 5, are as follows: Formic (C_1), acetic (C_2), propionic (C_3), butyric (C_4), valeric (C_5), caproic (C_6), heptoic (C_7), caprylic (C_8), and nonylic (C_9).

The association of the fatty acids, or fat and wax acids, with well known fats and waxes is of particular interest. *Butyric acid* is associated with butter; *caproic acid* with coconut oil; *caprylic acid* with human fat; *capric acid* with coconut fat; *lauric acid* with palm kernel and sperm head oil; *myristic acid* with spermaceti, coconut oil and wool wax; *palmitic acid*

Table 5. Solid Straight-Chain Saturated Fat and Wax Acids

N-Acid	$C_nH_{2n}O_2$	M. P. (°C)	B. P. (°C)	Density/°C
Capric	$C_{10}H_{20}O_2$	31.4	269/760 mm	0.8858(40)
Undecylic	$C_{11}H_{22}O_2$	28.0	284/760 mm 228/160 mm	0.8889(30)
Lauric	$C_{12}H_{24}O_2$	43.8	225/100 mm 130.5/1 mm	0.8744(45)
Tridecylic	$C_{13}H_{26}O_2$	40.5	236/100 mm	0.8458(80)
Myristic	$C_{14}H_{28}O_2$	54.4	250/100 mm 149/1 mm	0.8533(70)
Pentadecylic	$C_{15}H_{30}O_2$	52.1	266/100 mm	0.8423(80)
Palmitic	$C_{16}H_{32}O_2$	62.9	215/15 mm 167/1 mm	0.8500(68)
Margaric	$C_{17}H_{34}O_2$	61.3	224/15 mm	0.8396(80)
Stearic	$C_{18}H_{36}O_2$	69.9	303/100 mm 232/15 mm 160/1 mm	0.8325(100)
Nonadecylic	$C_{19}H_{38}O_2$	69.0	249/15 mm	——
Arachidic	$C_{20}H_{40}O_2$	75.4	328/100 mm 205/1 mm	0.8240(100)
Medullic	$C_{21}H_{42}O_2$	75.0	——	——
Behenic	$C_{22}H_{44}O_2$	81.0	306/60 mm	0.8221(100)
Lignoceric	$C_{24}H_{48}O_2$	85.0		0.8207(100)
Hexacosanic	$C_{26}H_{52}O_2$	87.7		0.8198(100)
Octacosanic	$C_{28}H_{56}O_2$	90.9		0.8191(100)
Triacontanic	$C_{30}H_{60}O_2$	93.6		0.8085(100)
Lacceric	$C_{32}H_{64}O_2$	96.2		
Tetratriacontanic	$C_{34}H_{68}O_2$	98.2		
Hexatriacontanic	$C_{36}H_{72}O_2$	99.9		
Octatriacontanic	$C_{38}H_{76}O_2$	101.6		
Tetracontanic	$C_{40}H_{80}O_2$	103.5		
Hexatetracontanic	$C_{46}H_{92}O_2$	115.0 (107.1)		

with many vegetable oils and waxes; *stearic acid* with beef fat; *arachidic acid* with peanut oil; *behenic acid* with oil of ben; *lignoceric acid* with many seed fats, and with rotten oak wood; *carnaubic* (isomer of lignoceric) and *myricinic acids* with carnauba wax; *cerotic, montanic* and *melissic acids* with beeswax; *lacceric acid* with "stick-lac"; and *geddic acid* with Ghedda wax. *Carbocerotic acid* ($C_{27}H_{54}O_2$ m. 82.5°) is found in Chinese insect wax.

Francis, King, and Willis[2] prepared a saturated monobasic acid with as many as 46 carbon atoms, *viz., hexatetracontanic acid* [$H(CH_2)_{45} \cdot COOH$ m. 115°]. The *hexatriacontanic acid* [$H(CH_2)_{35} \cdot COOH$] which they prepared melted at 99.9°. The melting points of these saturated fatty acids rise in direct proportion to the increase in the number of carbon atoms.

In the unsaturated fatty acids, or poly-ethanoid acids as they are now called, the melting point decreases with the number (increase) of double bonds, but both the specific gravity and the index of refraction increase. Most of the higher members of the series are found in the marine oils and in vegetable drying oils. They are seldom constituents of waxes, except the so-called liquid waxes, and as minor components in the form of glycerides in waxy matters extracted from plant material.

Table 6. Forked-Chain Isomers of the Saturated Monobasic Acids (Wax Series) $C_nH_{2n}O_2$

N-Acid	Formula	M.P. (°C)	Isomer	M.P. (°C)
Behenic	$C_{22}H_{44}O_2$	81.0	Isobehenic	75.5[a], 76.5[b]
Tricosanic	$C_{23}H_{46}O_2$	80.0		
Lignoceric	$C_{24}H_{48}O_2$	85.0	Pisang-ceric Iso-lignoceric[d] Carnaubic	71.0 73.5 72.5, 72[c]
Pentacosanic	$C_{25}H_{50}O_2$	84.0	Hyaenic, Cerotic (*a*)[e] Neocerotic	78 or 77.8
Hexacosanic	$C_{26}H_{52}O_2$	87.8	Cerotic (*b*)[f] Lanocerotic Pseudocerotic	79–81 78 83[g]
Heptacosanic	$C_{27}H_{54}O_2$	87.0	Carbocerotic, Cerotic(*c*)[h] Isocerotic, carboceric[j]	82.5[i] 82.0
Octacosanic	$C_{28}H_{56}O_2$	91.0	Neomontanic[k] Pseudomontanic	86 83
Nonacosanic	$C_{29}H_{58}O_2$	90.3	Montanic	86.8[l], or 85.0[m]
Triacontanic	$C_{30}H_{60}O_2$	93.6	Myricinic	86.0
Hentriacontanic	$C_{31}H_{62}O_2$	92.8	Melissic[n]	90, 91
Lacceric	$C_{32}H_{64}O_2$	96.0	Psyllic[o] Iso-lacceric[p]	94 89
Triatriacontanic	$C_{33}H_{66}O_2$	95.3	Ceromelissic	93.5, 94.0[q]
Tetratriacontanic	$C_{34}H_{68}O_2$	97.8	Geddic	94.9
Pentatriacontanic	$C_{35}H_{70}O_2$	97.0	Ceroplastic	96[q]

[a] M.p. by Meyer; [b] by Shriner; [c] by Betrabet; [d] Brigl; [e] refers to the C_{25} acid (neocerotic of Gascard); [f] refers to the C_{26} acid of Henriques; [g] m.p. by Damoy; [h] refers to the C_{27} acid of Brodie who discovered it; [i] m.p. by Gascard; [j] by Tropsch; [k] by Ludecke; [l] by Tropsch; [m] by Meyer; [n] named by Gascard; [o] of Sundwik; [p] m.p. by Holde; [q] by Koyama.

Identification of Cerotic Acid. The identification of what does and what does not constitute cerotic acid in the natural waxes has always been a subject of considerable discussion. A review of the history of the cerotic acids was given by Francis *et al.*[3] Brodie in 1848 considered that cerotic acid has a carbon content of 27. Schalfejew in 1876 confirmed that view, but found the presence of another acid in beeswax with a carbon content of 34 and a melting point of 91°. Nafzger[13] in 1884 concluded that the acid of beeswax was chiefly composed (excluding combined palmitic acid) of one with a carbon content of either 26 or 27, and that the higher acid present was either C_{30} or C_{31}. Marie in 1896 contended that the cerotic acid in question was really mixed with melissic acid, the former ($C_{25}H_{50}O_2$) melting at 77.9° and the latter ($C_{31}H_{62}O_2$) at 90.° In 1897 Henriques put forth his claim that cerotic acid, 78.5°, is unquestionably $C_{26}H_{52}O_2$, which view is now generally accepted, with certain reservations. Kiesel[6] in 1925 thought the values of the melting points given for cerotic acid were too low. He attempted to isolate cerotic acid from the spores of two species of ferns, and found that the acids melted at 85 to 85.5°, a closer approach to the melting point of synthetic C_{26} acid (see p. 20).

The difficulty of isolating the C_{26} acid from its homologs forming dimeric acids is illustrated by the following. Francis, Piper, and Malkin[3] in 1930 studied cerotic acid isolated from beeswax and prepared it by oxidation of paraffin wax and *n*-triacontane. They also prepared cerotic acid from carnauba wax and from Chinese insect wax. The acids of the beeswax had been converted into their methyl esters and fractionated, the fraction boiled between 245° and 255° at 3 mm, melted at 58°, and gave an acid which, after crystallization twice from carbon tetrachloride, melted at 77.5°. Repurification resulted in a melting point of 78.5°. Cerotic acid prepared from paraffin had a melting point of 80°. Acids obtained from carnauba wax had melting points of 76.5° to 81°; those from Chinese insect wax melted at 82.5° after purification (see p. 63).

Melting Point Depressions of Homologs of Fat and Wax Acids. When one fatty acid is mixed with another, the melting point of the mixture is lower than that of the lower-melting constituent, the acids forming a sort of eutectic. For example, C_{14} acid melts at 48.3° and C_{15} acid at 51.4°; but the mixture of unimolar weights of these two acids melts at 42.6°. This differential is symbolized in the literature as Δ m.p.; in the case of lower acid mixtures of C_n with C_{n+1} acids, this value is about 3° to 6°, when the lower-melting acid has an even number of carbons; there is little or no differential when the lower-melting acid has an odd number. The Δ m.p. for mixtures of C_n with C_{n+2} acids is about 4° to 6°, when the lower-melting acid has an even number of carbons; it is 2.5° to 5° when the lower-melting or lower homolog acid has an odd number of carbon atoms. For example, C_{18} is 70.1° m.p., and C_{20} is 75.1° m.p., the mixture of C_{18} and C_{20} in unimolar weights actually melts at 64.6°, or Δ m.p. is 5.5°. However, for C_{19} and C_{21} it is only 2.5°.

According to this reasoning, were there unimolar mixtures of the *n*-acids *pentacosanic* (m. 84°) and *heptacosanic* (m. 87°), we would have an acid of C_{26} formula that would have a melting point of about 80°, which is more or less the melting point of cerotic acid.

Hilditch[5a] says that the tendency for the different fatty acids to form an equivalent complex is readily understood when we remember that the crystal unit of the solid fatty acids has been definitely shown by x-ray analysis to be made up of two molecules of fatty acid apparently arranged with their free acidic groups oriented toward each other, whereas the esters of the acids are monomolecular in the solid state. There is some evidence to show that the liquid (unsaturated) higher fatty acids also pass into a bimolecular form. (The crystal cell of the saturated acid has four molecules. The dimer referred to has a hybrid. See p. 23).

Unsaturated Aliphatic Acids. Unsaturated acids play an insignificant role in the chemistry of waxes as contrasted to their great importance in the chemistry of oils. This is largely because unsaturated wax acids (of over 24 carbon atoms) are substantially non-existent; therefore we must look to the liquid waxes for the presence of the unsaturated fat acids in significant amounts. In the acrylic series, $C_nH_{2n-2}O_2$, *oleic acid,* is commonly found in very small amounts in vegetable waxes, and in larger amounts in the marine oils, quite a few of which are considered as liquid waxes. When oleic acid is carefully oxidized it yields *pelargonic acid* [$CH_3 \cdot (CH_2)_7 \cdot COOH$] and *azelaic acid* [$HOOC \cdot (CH_2)_7 \cdot COOH$], and hence the constitutional formula of oleic acid must be $CH_3(CH_2)_7 \cdot CH : CH(CH_2)_7 \cdot COOH$. Oleic acid crystallizes in needles, (m. 13.3°) and oxidizes with alkaline permanganate to *dihydroxystearic acid.* Oleic acid on reduction

Table 7. Unsaturated Aliphatic Acids

	Normal	Isomers
$C_{10}H_{18}O_2$	9-decenoic, m. < 0°, b$_4$ 142°	obtusilic (4-decenoic) 7-decenoic (of sperm oil)
$C_{11}H_{20}O_2$	9-hendecenoic, m. 24.5°, b. 260° $CH_3 \cdot CH : CH(CH_2)_7 \cdot COOH$	
$C_{12}H_{22}O_2$	lauroleic, m. 12°, b.$_{15}$ 135°	3-dodecenoic linderic (4-dodecenoic), m. 1.2° 11-dodecenoic, m. 19°, b$_{11}$ 139°
$C_{13}H_{24}O_2$	9-tridecenoic	12-tridecenoic, m. 38°, b$_{15}$ 185°
$C_{14}H_{26}O_2$	myristoleic (of marine oils)	5-physeteric (of sperm oil) tsuzuic (4-tetradecenoic), m. 20°
$C_{15}H_{28}O_2$	9-pentadecenoic	13-pentadecenoic, m. 42° 14-pentadecenoic, m. 50°, b$_8$ 195°
$C_{16}H_{30}O_2$	palmitoleic, m. 33° (of jojoba oil) (stable form m. 41°)	hypogaic (2-hexadecenoic), m. 60° gaidic (*trans*-9-hexadecenoic), m. 30° physetoleic, m. 30° (of sperm oil) lycopodic
$C_{18}H_{34}O_2$	oleic, m. 13.3° (stable form m. 16.3°)	petroselenic (6-octadecenoic), m. 34° elaidic (*trans*-9-octadecenoic), m. 51–52° elaidinic (10-octadecenoic), m. 43.7° vaccenic (11-octadecenoic), m. 40° 13-octadecenoic, m. 41–43° petroselidinic, m. 52.7° cheiranthic, m. 30° doeglic, m. 4° (of marine oils)
$C_{19}H_{36}O_2$	jecoleic	17-nondecenoic
$C_{20}H_{38}O_2$	9-eicosenoic, m. 68° (of jojoba oil)	*cis*-gadoleic, m. 24.5° (*trans*-m. 53–54°) isogadoleic, m. 65.8° gondoic, m. 32.5–24° (marine oils)
$C_{22}H_{42}O_2$	isoerucic, m. 54.8° (of rapeseed oil)	cetoleic (11-docosenoic) erucic (*cis*-13-docosenoic), m. 33.8° brassidic (*trans*-13-) m. 60.8° (stable form m. 65–66°)
$C_{24}H_{46}O_2$	9-tetracosenoic	*cis*-5-tetracosenoic, m. 70.6° *trans*-5-tetracosenoic, m. 41.1° *cis*-selacholeic (15-tetracosenoic), m. 44-45° *trans*-selacholeic, m. 66–67°.

yields *stearic acid.* *Palmitoleic acid,* the C_{16} acid, behaves like oleic acid. This acid is also referred to as *hypogoeic,* and crystallizes in needles (m. 33°); it is oxidizable in air, forming volatile acids of a rancid odor. *Elaidic acid* (C_{18}) crystallizes from ethanol in leaflets. *Iso-oleic* crystallizes from ether in transparent tablets (m. 44–45°). *Erucic acid* (C_{22}) crystallizes in long needles from ethanol. *Linoleic acid,* the C_{18} acid with two double bonds, and *linolenic* with three double bonds often accompany oleic acid in fruit and flower waxes.

Steroisomerism of Acids. In the monoethylenic series, isomers are plentiful because of the shifting of the double bond which takes place, often by the mere application of gentle heat, and also because of the steroisomerism (*cis-trans*) at the position of the double bond.

Table 7 arbitrarily lists the *cis*-9 acids as normal, and refers to the others as isomers.

Dibasic Acids

Dibasic acids of high molecular weight, are not often encountered in waxes, but they do play an important part in plant metamorphosis, as do the dihydric alcohols from which they are derived. With the loss of CO_2 they occur as wax acids, but occasionally as esters as in japan wax. The dibasic acids are solid, crystalline compounds of strongly acid character and are partially soluble in water. When heated, they either yield an anhydride, or carbon dioxide is liberated with the formation of a monobasic acid. Most of the dibasic acids can be volatilized *in vacuo.*

The behavior of the dibasic acids with an odd number of carbons differs from that of the even-numbered acids. In scanning the series of acids enumerated in Table 8 it will be at once apparent that the melting point of the first odd-acid is fairly low, and that the melting points gradually increase with each succeeding odd-acid, whereas with the even-acids the first acid starts with a high melting point and the melting points rapidly descend as we go up in the series. This causes the series to converge at about 123, with acids of 32 or less carbon atoms. The higher molecular acids become increasingly unstable to heat. An explanation of the phenomenon is to be found to some extent in the nature of the crystal cell of the dibasic acids.

The unit cell crystal spacings of the dibasic acids, as determined by Caspari by the x-ray rotating or oscillating crystal method, show that the acids with an even number of ethylenic (CH_2) groups have two moles to the crystal cell, whereas the odd-numbered acids have four moles tightly packed. The unit cells have nearly constant *a* and *b* axes; as regards the *c* axis, the acids fall into two groups, one having the moles of an even number of C atoms, the other those of an odd number. The *c* axis of the even-

Table 8. Saturated Dibasic Acids

Name	$C_nH_{2n-2}O_4$	Chain length (Å.U.)	M. P. (°C)	B. P. (°C)
Glutaric	$(CH_2)_3\cdot(COOH)_2$	——	97.5	304/760 mm
Adipic (1-4 butane dicarboxylic)	$(CH_2)_4\cdot(COOH)_2$	10.02 (1)	153.0	265/100 mm
Pimelic	$(CH_2)_5\cdot(COOH)_2$	22.12 (2)	105.5	272/100 mm
Suberic	$(CH_2)_6\cdot(COOH)_2$	12.58 (1)	140.0	279/100 mm
Azelaic	$(CH_2)_7\cdot(COOH)_2$	27.14 (2)	108.0	360/760 mm 237/215 mm
Sebasic (decandioic 1 : 10)	$(CH_2)_8\cdot(COOH)_2$	15.02 (1)	133.0	295/100 mm 243/15 mm
Undecandioic	$(CH_2)_9\cdot(COOH)_2$	——	110.0	
Dodecandioic	$(CH_2)_{10}\cdot(COOH)_2$	——	129.0 (125.5)	
Brassylic	$(CH_2)_{11}\cdot(COOH)_2$	37.95 (2)	112.5	
Tetradecandioic	$(CH_2)_{12}\cdot(COOH)_2$	——	126.5 (121.0)	
Pentadecandioic	$(CH_2)_{13}\cdot(COOH)_2$	——	113.5 (computed)	
Thapsic (tetradecane dicarboxylic)	$(CH_2)_{14}\cdot(COOH)_2$	——	125.0	
Roccelic	$(CH_2)_{15}\cdot(COOH)_2$	——	115.0	
Octadecandioic	$(CH_2)_{16}\cdot(COOH)_2$	25.10 (1)	124.0	
Nonadecandioic	$(CH_2)_{17}\cdot(COOH)_2$		116.5	106/0 mm
Eicosandioic	$(CH_2)_{18}\cdot(COOH)_2$		124–5	113/0 mm
Japanic (nonadecane-1,19-dicarboxylic)	$(CH_2)_{19}\cdot(COOH)_2$		117.5 (113.0) (118–120)	117/0 mm
Docosandioic (eicosane dicarboxylic)	$(CH_2)_{20}\cdot(COOH)_2$		123.5 (126) (124–5)	
Tricosandioic	$(CH_2)_{21}\cdot(COOH)_2$		118.5	
Tetracosandioic	$(CH_2)_{22}\cdot(COOH)_2$		123.0 (127.0)	
Carnaubandioic	$(CH_2)_{23}\cdot(COOH)_2$		102.5 (isomer)	
Hexacosandioic	$(CH_2)_{24}\cdot(COOH)_2$		123.0	
Octacosandioic	$(CH_2)_{26}\cdot(COOH)_2$		123–5	278/15 mm
Dotriacontandioic (1, 32)	$(CH_2)_{30}\cdot(COOH)_2$		123*	

* D. A. Fairweather, *Proc. Roy. Soc. Edinburgh*, **45**, 283–5 (1925).

numbered moles is proportional in length to the number of C atoms; for the odd-numbered moles it is proportional to twice the number of C atoms. In the latter group, two molecules lie end to end in the cell along the *c* axis. Examples of the unit cell construction are:

Acid	Å.U. length (10^{-8} cm)			β-angle	Moles per unit cell
	a	*b*	*c*		
C_{10} Sebasic	10.05	4.96	15.02	133° 50′	2
C_{13} Brassylic	9.63	4.82	37.95	128° 20′	4
C_{18} Octadecandioic	9.76	4.92	25.10	131° 10′	2

Mean difference of 1.53 Å.U. between carbons

The dibasic acids listed in Table 8 are normal, but many isomers exist. Generally speaking, those acids having 15 or more carbons are the ones occurring in waxes. The first of these is $(CH_2)_{13}\cdot(COOH)_2$, *a dibasic acid*, also referred to as triadecamethylenedicarboxylic or pentadecandioic acid; it has two well known isomers: diisobutyl pimelic and diisoamyl glutaric acids. The C_{16} acid, *thapsic*, has an isomer, as do *roccelic* and octadecandioic. *Nonadecandioic* $[(CH_2)_{17}\cdot(COOH)_2]$ has two isomers, cetyl malonic and dioctyl malonic. *Japanic acid* has an isomer known as octadecyl malonic. The C_{22} acid is known only in the normal state, whereas the C_{23} acid occurs only in the isomeric state, eicosyl malonic acid. The C_{24} acid is known as the isomer, didecyl succinic acid. The C_{25} acid, *carnaubandioic*, is reported as having been obtained by the oxidation of the dihydric alcohol, $C_{25}H_{52}O_2$, from *carnauba wax*, but its structure has not been fully established. The C_{27} acid is an isomer known as tetracosylmalonic acid Higher acids are known, *e.g.*, a C_{35} acid (dicetyl malonic) and a C_{38} acid (dicetyl adipic acid), which are isomers.

Unsaturated dibasic, hydroxy dibasic, dihydroxy dibasic, and polyhydroxy dibasic acids, are more closely allied with sugars and starches, and are rarely encountered in waxes. *Shellolic acid* and similar acids found in shellac and present in shellac wax as an impurity are hydroxy derivatives of the unsaturated dibasic acids of very high molecular weight.

Hydroxy Acids. Aliphatic monohydroxy and dihydroxy acids are not uncommon constituents of the natural waxes. Trihydroxy acids are found occasionally. Acids having less than 8 carbon atoms do not occur in waxes, not even liquid ones. When the hydroxy (OH) group adjoins the COOH group, the acid is called an α-hydroxy acid, if it adjoins the first CH_2 group which is attached to the COOH it is called a β-hydroxy acid; if it is one position still farther removed it is called a γ-hydroxy acid. When the OH group is terminal, the hydroxy acid (ω-hydroxy acid) acts as an alcohol as well as an acid. This latter type plays an important role in the metabolism changes in the conifers, and is to be found in the waxes of conifers accompanied by a corresponding lactone. The γ and δ hydroxy acids are quite unstable and split off a molecule of water readily to form lactones.

It is simpler to designate the position of the OH group by a number than by letter of the Greek alphabet. If the first carbon, namely that of the COOH group, be designated as 1, then α-hydroxy becomes 2-hydroxy; β-hydroxy, 3-hydroxy, and so on.

The dihydroxy acids have in the past been designated by Greek letter prefixes as to the position of the OH groups, but are now commonly designated by numbers. Number 1 position is assigned to the carbon of the COOH group; hence 2,3,-dihydroxy denotes that the attachment of the OH groups is at the two carbon atoms directly adjoining the COOH group. Dihydroxyacids generally result from the saponification of unsaturated fatty acids, or are formed when such acids have been oxidized. As a rule, the melting points increase with the number of oxygens introduced in the molecule, for example:

$$\underset{\text{m. }69.6^\circ}{\text{stearic}} \rightarrow \underset{\text{m. }91.5^\circ}{\text{2-hydroxystearic}} \rightarrow \underset{\text{m. }117.5^\circ}{\text{6,7-dihydroxystearic}} \rightarrow \underset{\text{m. }141^\circ}{\text{trihydroxystearic}} \rightarrow$$

$$\rightarrow \underset{\text{m. }163.5^\circ}{\text{tetrahydroxystearic(sativic)}} \rightarrow \underset{\text{m. }203.5^\circ}{\text{hexahydroxystearic(linusic)}}$$

An example of a trihydroxy acid is *aleuritic* acid, a constituent of shellac wax. Aleuritic acid corresponds to 9, 10, 16-trihydroxypalmitic acid.

Table 9. Higher Hydroxy and Dihydroxy Acids

Total Number of Carbons	Monohydroxy Acids $C_nH_{2n}(OH)\cdot COOH$	M. P. (°C)	Dihydroxy Acids $C_nH_{2n-1}(OH)\cdot COOH$	M. P. (°C)
(9)	2-hydroxynonanic	63		
	3-hydroxynonanic	51, 48		
	9-hydroxynonanic	51.5		
(10)	2-hydroxydecanic	67	2,3-dihydroxydecanic	121
	3-hydroxydecanic	68		
	10-hydroxydecanic	65		
(11)	2-hydroxyundecanic	72	dihydroxyundecanic	84–6
	4-hydroxyundecanic	34		
	11-hydroxyundecanic	76		
(12)	2-hydroxydodecanic	76	2,3-dihydroxydodecanic	115.2
	3-hydroxydodecanic		4,5-dihydroxylinderic	102
	4-hydroxydodecanic	63		
	12-hydroxydodecanic (sabinic)	84		
(13)	2-hydroxytridecanic	79		
	4-hydroxytridecanic	66		
	11-hydroxytridecanic	28.5		
	13-hydroxytridecanic	79.3		
(14)	2-hydroxymyristic	82	dihydroxymyristic (ipurolic)	127.5
	3-hydroxymyristic			
	4-hydroxymyristic	34	5,6-dihydroxymyristic	118–9
	14-hydroxymyristic	91		
(15)	2-hydroxypentadecanic	84.5	4,12-dihydroxypentadecanic	
	4-hydroxypentadecanic	51		
	10-hydroxypentadecanic	63.7		
	11-hydroxypentadecanic	70.5		
	15-hydroxypentadecanic	84–5		
(16)	2-hydroxypalmitic	86.5	2,3-dihydroxypalmitic	126
	3-hydroxypalmitic	83.5	3,12-dihydroxypalmitic	83.4
	4-hydroxypalmitic	29?	7,8-dihydroxyhypogaic	115
	7-hydroxyhypogaic	34	*cis*-9,10-dihydroxypalmitic	89.5
	10-hydroxypalmitic	63.7	*trans*-9,10-dihydroxypalmitic	124.5
	11-hydroxypalmitic	68.5	7,16	83–4
	16-hydroxypalmitic (juniperic)	95 (92–93)		
(17)	2-hydroxymargaric	89	2,3-dihydroxymargaric	127–130
	4-hydroxymargaric	58?		
	17-hydroxymargaric	87.7		
(18)	2-hydroxystearic	91	2,3-dihydroxystearic	126
	3-hydroxystearic	85	*cis*-6,7-dihydroxystearic	117.5
	4-hydroxystearic	47.5	*trans*-6,7-dihydroxystearic	122
	5-hydroxystearic	54.5	*cis*-7,8-dihydroxystearic	96.5
	6-hydroxystearic	58?	*cis*-9,10-dihydroxystearic	98
	7-hydroxystearic	63?	*trans*-9,10-dihydroxystearic	132
	8-hydroxystearic	?	*cis*-9,12-dihydroxystearic	90
	9-hydroxystearic	74.5	10,12-dihydroxystearic	116
	10-hydroxystearic	81–2		
	11-hydroxystearic	76–7		
	12-hydroxystearic	78–9		
	13-hydroxystearic	77–77.5		
	14-hydroxystearic	76.5		
	16-hydroxystearic	87?		

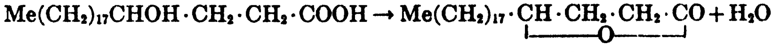
Table 9. Higher Hydroxy and Dihydroxy Acids—(*Continued*)

Total Number of Carbons	Monohydroxy Acids $C_nH_{2n}(OH)\cdot COOH$	M. P. (°C)	Dihydroxy Acids $C_nH_{2n-1}(OH)\cdot COOH$	M. P. (°C)
	18-hydroxystearic	97		
(19)	2-hydroxynondecanic	93	dihydroxyjecoleic	128
	4-hydroxynondecanic			
	19-hydroxynondecanic	92(91-91.5)		
(20)	2-hydroxycosanic	94	dihydroxygadoleic	128
	3-hydroxycosanic	?		
	20-hydroxycosanic	97.6		
(21)	2-hydroxyuncosanic	96		
	4-hydroxyuncosanic	?		
	21-hydroxyuncosanic	92.7		
(22)	2-hydroxydocosanic (phellonic)	96.5	2,3-dihydroxybehenic *cis*-13,14-dihydroxybehenic	132-3 99-101
	3-hydroxycosanic	?		
	22-hydroxycosanic	98		
(24)	2-hydroxytetracosanic	98-9.5		
	3-hydroxytetracosanic	?		
	24-hydroxytetracosanic (carnaubanoic)	?		
(26)	2-hydroxycerotic	102		
(28)	2-hydroxyoctacosanic	104		
(30)	2-hydroxycontanic	106	dihydroxymyricinic (lanoceric)	140
(31)	2-hydroxyuncontanic (cocceric)	110		
(32)	2-hydroxycontanic	108		
(33)	33-hydroxytriacontanic (pemphygic)	101-2		
(34)	2-hydroxytetratriacontanic	109-10		

NOTE: 3-hydroxy acids with odd number of ten or more carbons if formed are unstable and revert to corresponding γ-monoethylenic acids. The 34-α acid crystallizes from benzene with m.p. of 109-110°, but on solidification melts at 104-105°, crystal spacing 77 Å.U.

Lactones

The γ- and δ-hydroxy acids lose a mole of water at ordinary tempertures, and change more or less completely into simple cyclic esters, the γ- and δ-lactones. The α- and β-hydroxy acids do not so change. In the formation of lactones of the anolide type, the carboxy (COOH) group enters into reaction with the hydroxy (OH) group, splitting off a mole of water and forming an anhydride.



$$Me(CH_2)_{17}CHOH\cdot CH_2\cdot CH_2\cdot COOH \rightarrow Me(CH_2)_{17}\cdot \underbrace{CH\cdot CH_2\cdot CH_2\cdot CO}_{O} + H_2O$$

γ-hydroxybehenic acid *γ-behenolactone*

Unsaturated acids in which the double union occurs in the β, γ or γ,δ position yield lactones by heat alone.

The higher γ saturated lactones are solid, *e.g.*, γ-myristo-lactone (1,4-tetra-decanolide, m. 29°) is accredited as a constituent of beeswax. 1,4-pentadecanolide melts at 32°. These lactones are fragrant, the 1,4-undecanolide ($C_{11}H_{20}O_2$) having a strong peach-like odor.

The monocyclic lactones (ω-1-lactones) occur in dimeric and trimeric as well as monomeric form. The monomeric lactones have a low melting point, the longer-chain lactones much higher ones. The C_{10} lactone (monomeric) boils at 67–75°/8.3 mm and melts at 4–5°; C_{12} lactone $b_{0.25}$ 88–90°, m. 26°; C_{14} lactone b_{15} 176°, m. 41–2°; C_{15} lactone b_{15} 188°, m. 35–6°; C_{16} lactone, b_{15} 194°, m. 41–2°; C_{17} lactone, $b_{0.2}$ 135–8°; C_{18} lactone $b_{0.15}$ 136–8°, m. 51.2° (also reported as low as 36–7°); C_{23} lactone $b_{0.2}$ 174–6°, m. 35–6°; C_{24} lactone m. 69–70°.

The C_{22} lactone (*behenolactone*) is reported to have a melting point of 63.5°; the C_{26} lactone (*cerotolactone*) melts at 76°; and the C_{30} lactone (*myricinolactone*) melts at 88°. The latter is a constituent of candelilla wax, and also appears identical with *lanocero-lactone* derived from wool grease. The *stearo-lactone* of candle material has been reported as having a melting point of 49°. It is probably a mixture of the monomer, m. 36–7°, and the dimer, m. 113–4°.

Wax Esters

Alkyl esters resulting from the union of the higher aliphatic alcohols, and less often with the cyclic alcohols such as the sterols, are the principal components of the natural waxes. In the metabolism of the organisms of nature there appears to be a close relationship of equilibrium between acid, alcohol, ester and hydrocarbon, the latter as an end residue. Hence we may expect to encounter all four components in many of the waxes, although where there is an excess of acid constituents the amount of alcohols is substantially nil. When the free acid content is exceedingly low there is usually a substantial amount of free alcohols. Esters are monomeric, not dimeric, as are the acids and alcohols. The esters encountered in nature always have an even number of carbon atoms, although it is uncertain whether this rule follows for esters having an extremely high molecular weight. There is apparently a tendency for an acid of odd carbons to combine with an alcohol of odd carbons to form an ester of an even number of carbons, *e.g.*,

$$\underset{\textit{montanic acid}}{C_{28}H_{57}\cdot COOH} + \underset{\substack{\textit{montanyl}\\ \textit{alcohol}}}{HO\cdot C_{29}H_{59}} \rightarrow \underset{\textit{montanyl montanate}}{C_{28}H_{57}\cdot CO\cdot OC_{29}H_{59}} + \underset{\textit{water}}{H_2O}$$

The esters of high molecular weight formed by metamorphosis in nature are extremely difficult to reproduce in the laboratory. For purposes of identification the acids isolated from waxes can be readily converted to ethyl or other low alkyl esters, and then separated by distillation and recrystallization. The combining weight of an acid, together with the melting point, may determine whether the unknown is an acid or a hybrid mixture of homologs of the acid, since a mixed dimer will have a much lower melting point than would otherwise be the case. The boiling points obtained in a fractional molecular distillation of the lower alkyl esters are also a means of identification. (See Table 10.)

Melting Points of Alkyl Esters of Palmitic and Stearic Acids. Whitby[19] has given the following melting-point constants for the synthetically prepared esters of palmitic and stearic acids, except methyl esters, which are by Niemann[14], and the value for *n*-decyl palmitate.

	M. P. (°C)	
	Palmitic	Stearic
methyl	29.0	37.0
ethyl	23.5	33.6
propyl	20.4	30.5
butyl	16.9	27.5
amyl	19.4	30.0
iso-amyl	12.5	23.0
octyl	22.5	31.8
decyl	30.0	—
cetyl	51.6	56.5

The melting points of the alkyl esters rise with an increase in the number of acyl carbon atoms, and decrease somewhat with an increase in the molar weight of the alkyl group, *e.g.*, *methyl stearate* melts at 37°, but *methyl montanate* melts at 66°; *ethyl montanate* melts at 64–65°, and *propyl montanate* at 63.5°.

Methyl montanate may be prepared by boiling montanic acid with methanol in the presence of sulfuric acid. The resulting montanate can be crystallized in the form of curved needles.

Index of Refraction at 45° for Methyl Esters of the Higher Fatty Acids:
Values by Wyman and Barkenbus

methyl caprylate	1.4069	methyl myristate	1.4281
methyl caprate	1.4161	methyl palmitate	1.4317
methyl laurate	1.4220	methyl stearate	1.4346

NOTE: methyl stearate was fractionated through a 10-plate Podbielniak column; methyl esters of caprylic, capric, lauric, and myristic through the spinning-band type of column. [*Ind. Eng. Chem.* (*Anal. Ed.*), 12, 658 (1940).]

Alkyl Esters of Wax Acids. Levene and Taylor[9] considered the published melting points of the ethyl esters of the monobasic acids a trifle low, and established new ones from synthetically prepared esters (C_{16} to C_{25}). Table 11 is based in part upon their figures and upon those of Francis. The melting points of the esters that have an odd number of carbon atoms in the acyl radical are staggered from those of an even number of carbons since, they fall on slightly different curves when plotted.

It is of interest to note that the boiling points of the esters fall in line, irrespective of whether the number of carbons is even or odd, which is, of

Table 10. Esters Occurring in Natural Waxes

Name of Ester	$C_{2n}H_{4n}O_2$* No. of Carbons Acyl R	 Alkyl R	M. P. (°C)	Molecular Weight
Cetyl laurate	C_{12}	C_{16}	41(C)	424.73
Lauryl myristate	C_{14}	C_{12}	32	396.68
Myristyl myristate	C_{14}	C_{14}	38	424.73
Cetyl myristate	C_{14}	C_{16}	48(C)	452.78
Ceryl myristate	C_{14}	C_{26}	62	593.04
Cetyl palmitate	C_{16}	C_{16}	51.6(W), 53(C)	480.83
Octadecyl palmitate	C_{16}	C_{18}	55	508.88
Ceryl palmitate	C_{16}	C_{26}	69	621.09
Myricyl palmitate	C_{16}	C_{30}	73	676.85
Melissyl margarate	C_{17}	C_{31}	79	705.25
Lauryl stearate	C_{18}	C_{12}	49	450.76
Cetyl stearate	C_{18}	C_{16}	55, 56.5(W)	508.88
Stearyl stearate	C_{18}	C_{18}	58.5(S), 62	536.93
Ceryl stearate	C_{18}	C_{26}	73(G)	649.14
Myricyl stearate	C_{18}	C_{30}	76(G)	705.25
Myricyl isobehenate	C_{22}	C_{30}	82	761.35
Ceryl carnaubate	C_{24}	C_{26}	81(G)(S)	733.30
Ceryl lignocerate	C_{24}	C_{26}	79	733.30
Myricyl tetracosanate	C_{24}	C_{30}	83	789.40
Carnaubyl cerotate	C_{26}	C_{24}	78.5	733.30
Ceryl cerotate (*b*,*b*)	C_{26}	C_{26}	84(D)	761.35
Myricyl cerotate (*b*)	C_{26}	C_{30}	87	817.46
Ceryl cerotate (*c*,*c*)	C_{27}	C_{27}	87	789.40
Montanyl cerotate	C_{27}	C_{29}	88	817.46
Melissyl cerotate	C_{27}	C_{31}	86	845.51
Tetracosyl neomontanate	C_{28}	C_{24}	84	761.35
Ceryl montanate (*c*)	C_{29}	C_{27}	87	817.46
Montanyl montanate	C_{29}	C_{29}	85, 89	845.51
Ceryl myricinate	C_{30}	C_{26}	87	817.46
Myricyl myricinate	C_{30}	C_{30}	87, 90.3	873.56
Ceryl melissate (*c*)	C_{31}	C_{27}	86(K)	845.51
Melissyl melissate	C_{31}	C_{31}	92.5, 90.5(G)	901.61
Myricyl laccerate	C_{32}	C_{30}	90, 92.5(G)	901.61
Lacceryl laccerate	C_{32}	C_{32}	92.5, 95(G)	929.66
Geddyl geddate	C_{34}	C_{34}	98	985.77

If the ceryl group is acyl or alkyl and has 25 C atoms it is referred to as (*a*); if 26 C atoms as (*b*); if 27 C atoms as (*c*).

(W) = Whitby, (S) = Shinozaki, (G) = Gascard, (D) = Damoy, (K) = Kono, (C) = Cataline.

*C_{2n} may be regarded as the total number of C atoms, that is, the sum of the C atoms in the acyl and alkyl radicals of the ester.

course, not true of the melting points. The above melting points are those of the acids crystallized from ethanol, the points being slightly different for the β-esters crystallized from a non-polar solvent such as benzene. It will be observed that the melting points of the methyl esters are higher than those of the corresponding ethyl esters, but as a rule this is not true of the boiling points. To illustrate, Toyama[18] reported *methyl behenate* to melt at 54–55°, and to boil at 224–225°; *ethyl behenate* to melt at 50–50.5°, and to boil at 230.1°

The interplanar x-ray crystal spacings of the alkyl esters show chain lengths which are monomolecular. This makes it possible to purify the

Table 11. Alkyl Esters of Wax Acids

Acyl Carbons	Acid	α-Methyl Ester M.P. (°C)	α-Methyl Ester B.P. (°C)	α-Ethyl Ester M.P. (°C)	α-Ethyl Ester B.P. (°C)
16	Palmitic	30.5	154/1 mm	24.2	
17	Margaric	29.7	170/1 mm	27.0	
18	Stearic	39.1	180/1 mm	33.6	152/0.18 mm
19	Nondecylic	39.3	188/5 mm	37.0	167/0.27 mm
20	Arachidic	46.6	206.5/5 mm	42.0	177/0.28 mm
21	Medullic	47.6	—	45.0	185/0.20 mm
22	Behenc	53.3	224/5 mm	49.0	192/0.22 mm
23	Tricosanic	54.4	—	52.0	199/0.27 mm
24	Lignoceric	58.4	242/5 mm	56.0	208/0.24 mm
25	Pentacosanic	60.0	—	58.9	216/0.50 mm
26	Hexacosanic	63.4	258/5 mm	60.0	199/0.30 mm
27	Heptacosanic	65.0	266/5 mm	61.5	
28	Neomontanic	67.4	270/5 mm	64.5	
29	Montanic	69.0	277/5 mm	66.6	
30	Myricinic	71.7	282/5 mm	69.0	
31	Melissic	74.5		71.4	
32	Lacceric	74.9		72.5	
33	Tritriacontanic	76.5*		75.0*	
34	Geddic	77.9		75.4	
35	Pentatriacontanic	79.0*		77.7*	
36	Hexatriacontanic	80.9		78.6	
37	Heptatriacontanic	—		—	
38	Octatriacontanic	83.1		80.5	
46	Hexatetracontanic	91.7		90.2	

* Koyama.

wax acids by preparing their ethyl and other alkyl esters, and then separating the esters by fractional distillation or by crystallization.

The melting points of the lower group of alkyl esters—methyl, ethyl, propyl, butyl—are helpful in identifying the acids esterified. These esters are never found as components of waxes. The melting points of the saturated fatty acids are substantially the same as those of the corresponding glycerides, for acids having 10 or more carbon atoms. This is shown in the following data:

	M. P. (°C) Fatty acids	M. P. (°C) Glycerides
Caproic	- 8.0	- 25.0
Caprylic	16.5	8.1
Capric	31.4	31.1
Lauric	43.6	45.7
Myristic	53.8	55.3
Palmitic	62.6	64.3
Stearic	69.3	71.6
Cerotic	77.8	76.8
Oleic	14.0	- 4.5 (solidifying point)
Erucic	33.5	31.0 (solidifying point)
Brassidic	63.0	47.0 (solidifying point)

Higher alkyl esters, such as the higher cetyl esters, can be synthesized in the following manner: equimolar amounts of *stearic acid* and *cetyl alcohol* are mixed at atmospheric pressure, and a current of carbon dioxide is passed through the mixture. The reaction begins at 220° and is complete in two hours. The temperature is increased to 270° to secure a 95 per cent yield of *cetyl stearate.*

Polymethylene Acid Alcohols. Hydroxy acids in which the OH group is at the end have both alcoholic and acidic properties; they are condensible to etholides in which the terminal OH and COOH groups combine, with elimination of water much in the same manner as in the formation of esters. For example, the etholide formed from 9-hydroxy nonanic acid is $CH_2(OH)(CH_2)_7CO_2 \cdot CH_2(CH_2)_7 \cdot COOH$ (m. 60°). This readily couples to form a double etholide (m. 71°):

$$HO_2C(CH_2)_7CH_2 \cdot O_2C(CH_2)_7CH_2 \cdot O_2C(CH_2)_7CH_2 \cdot O_2C(CH_2)_7 \cdot CH_2OH$$

Etholides are constituents of waxes from perfumed plants and conifers.

Table 12. Molecular Weights and Saponification Values of Glycerides

Name	Formula	Molecular Weight	Saponification Value
Laurin	$C_3H_5(O \cdot C_{12}H_{23}O)_3$	638.98	263.41
Myristin	$C_3H_5(O \cdot C_{14}H_{27}O)_3$	723.14	232.75
Palmitin	$C_3H_5(O \cdot C_{16}H_{31}O)_3$	807.29	208.49
Hydnocarpin	$C_3H_5(O \cdot C_{16}H_{27}O)_3$	795.20	211.66
Stearin	$C_3H_5(O \cdot C_{18}H_{35}O)_3$	891.45	188.81
Olein	$C_3H_5(O \cdot C_{18}H_{33}O)_3$	885.40	190.01
Linolin	$C_3H_5(O \cdot C_{18}H_{31}O)_3$	879.35	191.40
Chaulmoogin	$C_3H_5(O \cdot C_{18}H_{31}O)_3$	879.35	190.40
Linolenin	$C_3H_5(O \cdot C_{18}H_{29}O)_3$	873.31	192.73
Clupanodonin	$C_3H_5(O \cdot C_{18}H_{27}O)_3$	867.26	194.07
Ricinolein	$C_3H_5(O \cdot C_{18}H_{33}O_2)_3$	933.40	180.32
Arachin (Arachidin)	$C_3H_5(O \cdot C_{20}H_{39}O_2)_3$	975.61	172.52
Erucin (Behenin)	$C_3H_5(O \cdot C_{22}H_{41}O)_3$	1053.71	159.73
Cerotin	$C_3H_5(O \cdot C_{26}H_{51}O)_3$	1218.07	138.18
Myricin	$C_3H_5(O \cdot C_{30}H_{59}O)_3$	1396.38	120.53
Hydroxystearin	$C_3H_5(O \cdot C_{18}H_{35}O_2)_3$	939.44	179.16
Dihydroxystearin	$C_3H_5(O \cdot C_{18}H_{35}O_3)_3$	987.44	170.45
Trihydroxystearin	$C_3H_5(O \cdot C_{13}H_{35}O_4)_3$	1035.44	162.55
Sativin	$C_3H_5(O \cdot C_{18}H_{35}O_5)_3$	1083.44	155.35
Linusin	$C_3H_5(O \cdot C_{18}H_{35}O_7)_3$	1179.44	142.70

Melting points of some of the glycerides are as follows: laurin 45–46.4°; myristin 54–56.5°; palmitin 63–65.5°; stearin 71.6°; and cerotin 76.5–77°.

Hydroxy Alkyl Esters of Wax Acids. The ester of a hydroxy aliphatic saturated monocarboxylic acid of 16 to 24 carbon atoms and an aliphatic monohydric alcohol of similar carbon content has more of the properties of a natural wax than a similar ester prepared from an acid without the hydroxy group. An example is octadecyl 12-hydroxy stearate, m. 73°, which can be prepared, according to Snell and Guiteras,[16] by melting hydroxystearic acid with octadecyl alcohol, using *para*-toluene sulfonic acid as the activating agent, and then later washing out the catalyst and recrystallizing the product from warm alcohol. Similarly stearic acid and 1-12-octadecane diol give 12-hydroxy octadecyl stearate.

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Chapter 3

The Natural Waxes

Part I: Waxes from Insects

Classification and Social Order of Wax-producing Insects

The two principal groupings of the wax-producing insects are (1) the *Apidae*, of which the honey bees are the outstanding members; and (2) the *Coccidae* to which belong the *Coccus ceriferus*, the source of Chinese insect wax, and the *Carteria lacca*, source of stick-lac.

Apidae. Under the order *Apidae* there are three genera: (1) the genus *Apis* which is of the highest social order, producing the valuable combs of wax; (2) *Melipoma*, *Trigona* and *Tetrasoma*, all rather small and stingless bees, their brood cells resembling those of the common wasp, each forming but a single layer; (3) *Bombus*, which is otherwise known as the humble or "bumble" bee, which does not swarm like the other bees.

BEESWAX

Genus Apis

This is the genus which plays the most important economic role by furnishing the beeswax of commerce. Under the genus *Apis* we find a number of species: the giant bee, *Apis dorsata*; a medium sized bee, *Apis indica*, also of Asia; *Apis florea*, the tiny East Indian bee; and lastly the domesticated honey bee, *Apis mellifica*. The honey bee was originally named *Apis mellifera* by Linnaeus in 1758, although he changed the name later to *Apis mellifica* to denote the hive-bee specifically. The term *A. mellifera* is used in a more general sense to cover honey carriers or bearers. The *Apis mellifica* produce honeycombs of almost pure wax, referred to commercially as "genuine beeswax."

There are almost as many races of *A. mellifica* and its closely allied varieties as there are countries in which bees are domesticated—that is all over the world. There are for example, the black bees of Caucasia, Carniola and Banat; the brown bees of Great Britain and Continental Europe; the yellow bees indigenous to Cyprus, northern Italy, and the Holy Land, and generally propagated in the United States; all these exist in variants or strains with mixed colors. The refined waxes obtained from these races of *A. mellifica* differ little in their physical characteristics or chemical constants.

Besides the official species, other social bees are used as honey makers and wax producers, *e.g.*, *Apis facista* in Northern Africa, which inhabits the floating apiaries of the Nile, and is regarded as the prettiest bee in the world; *Apis adansonii* in Senegal; *Apis caffra* and *Apis scutelata* in Southern Africa; *Apis unicolor*, regarded as the blackest bee, a pure race domesticated in Madagascar and introduced in other parts of the world. The species in East India and the Orient produce a different kind of wax from those above mentioned; it is known as "Ghedda wax." These East Indian species, as previously mentioned, are *Apis dorsata*, *Apis florea*, and *Apis indica* (see Ghedda Wax p. 50).

Secretion of Wax by Bee. The wax scales are secreted by eight wax glands on the under side of the abdomen of the worker bee. When first secreted, the wax, which is derived from the blood of the bee by cell action, is liquid. The secretion rapidly hardens to a pearly scale, more or less transparent, like mica. The wax scale is removed from the abdomen by a hind leg of the insect, and received by the mandible of a co-worker, where it is chewed with a secretion, before placing the wax wafer in the cell of a comb. The comb is constructed to a hexagonal pattern (often a man-made beeswax foundation), which provides structural strength and maximum economy of space. In the natural comb there are 4.83 cells to the linear inch, or 825 cells to the square decimeter. The bees are believed to deploy about eight pounds of honey in order to secrete one pound of wax.

Rendering of Crude Beeswax. Crude beeswax is usually rendered from the frames and from scrapings by melting over hot water or under solar heat. In the hot-water extraction process the container is partially filled with boiling water, and the beeswax from broken combs or cappings added. It is common practice to soak the combs in cold water for several hours before melting, so that when the wax is melted over the boiling water it will not be absorbed by its impurities, and the water-soluble substances will be freely washed out. The melted wax floats on the surface, and is strained with the water through a wet cloth to remove bee and coccoon fragments and other foreign matter. Upon cooling, the wax solidifies into a cake on top of the water; dirt is removed by scraping the bottom of the cake. The straining can also be accomplished by dragging the mass with a cheesecloth fastened to a hoop, and permitting the wax to harden on cooling. The cake is then removed.

If the combs are rendered on a large scale the melted wax is removed from the hot-water container by decantation from the surface, any residue is placed in layers of straw and pressed to obtain more wax, the straw acting as a filter. A wax press employing hot water for this purpose is available on the market. The product so produced is "press wax." High- or low-pressure steam is a good indirect source of heat for melting wax. The water used in the melting process should have a low mineral content. Stainless steel or aluminum is desirable for wax-processing equipment. Wood or glass makes an excellent container for the manipulation of wax, which will become contaminated by the use of iron equipment.

In cleanups at wax-rendering plants benzene is used as a solvent for the wax, and the product resulting after evaporation of the benzene is known as "extraction wax," which is an impure form. Beeswax is generally molded in the shape of thick round cakes, but it may also be made in square and oblong cakes.

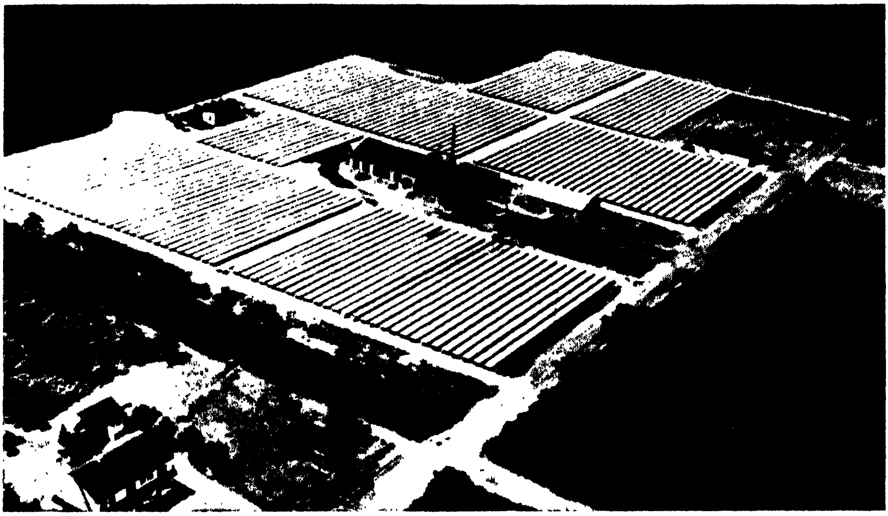


FIGURE 2. Koster Keunen sunbleached beeswax plant, Sayville, N. Y.

In the "solar extraction process" the crude wax from the cappings can be rendered by exposing it to the sun in a solar extractor. Sun melting reduces the intensity of its color and removes soluble contaminating substances by coagulation. Vansell and Bisson[143] state that one large producer in the Sacramento Valley of California, in preparing cappings for solar extraction, lets the cuttings fall into cloth boxes, which are supported over a long, shallow draining trough, thus allowing the cappings honey to run into the general stream from the extractor. As each box becomes filled, it is slid along the rack and replaced by an empty one. When the cappings are sufficiently drained of honey, each box is transferred to an individual solar extractor. A long, narrow extractor could be constructed to accommodate several of these boxes, thus increasing the efficiency of the process. Galvanized iron is a satisfactory construction material for the solar extractor.

In preparing the best quality of wax for commerce it is a common practice to pare off the capping of the honey cells and then place the comb in a centrifugal machine (extractor), which removes the honey and leaves the comb undamaged so that it can be replaced in the hive to be refilled by the bees, and thus save the honey they would use in making a new comb. Such a prepared wax is of a good grade as it is free from *propolis,* a greenish-brown, resinous substance that the bees use in sealing the cells in the comb and for attaching it to its support. The bees obtain the resin from the branches and leaves of the birch, ash, elm, balsam, poplar and other trees. When a comb has been refilled by the bees several times and is melted down, the wax is very brown, and strong in odor.

Comb foundations are provided for hive-bees so as not to waste honey; 1½ to 3 pounds of wax can be gotten from ten combs when they are scraped. The largest amount of wax is in the foundation and in the capping, since the side walls are remarkably thin.

Coloration of Beeswax. Vansell and Bisson[143] of the California Agricultural Experiment Station made a study of the coloration of beeswax. Freshly secreted beeswax is white, but it readily adsorbs colors from various sources. Some pollens carry yellow substances, which are liberated to the beeswax in either solid or liquid state. A cell in a new bee comb, as well as the walls of the adjacent cells, becomes very yellow when melted (in glass) with fresh pollens collected from various plants. It was found that color was liberated from pollen much more slowly after the grains had become dry. For example, the color imparted to white beeswax by the golden pollen of the sunflower, *Helianthus bolanderi,* is a bright orange yellow; that of the golden pollen of the California poppy a brilliant orange yellow; that of the bright yellow dandelion, *Taraxacum officinale,* Weber, a bright yellow; that of the brown pollen of the white clover, *Trifolium repens, L.,* only a trace of yellow; that of the pollens of alfalfa, flax, hollyhock, and many others, none.

Much of the crude beeswax imported from Cuba and other Caribbean countries is distinctly brown. It has a strong beeswax odor, masked to some extent by a tobacco-like smell. The pollen of tobacco plants is said to be responsible for both the off-odor and the off-color of this wax. Beeswax from South American sources is often lacking in pronounced color or odor, even though free from the adulteration by paraffin sometimes found in Chilean beeswax. Crude beeswax from West Africa has a strong yellow color and a strong beeswax odor, and comes characteristically blackened at the edges of the pieces. Some of these characteristics distinguish one sample of beeswax from another as to origin. A practice to be condemned is the artificial manufacture of comb foundations from hydrogenated castor oil, solid petroleum hydrocarbons, or other false waxes, as such foundations eventually find their way into the beeswax of commerce as undesirable impurities.

Sources of Supply of Beeswax. More than fifty years ago Herbig[60] attempted to show the world-wide distribution of beeswax in the following manner: Europe: Germany, Turkey, Italy, Portugal, and France. Africa: Egypt, East and West Africa. Asia: Syria, Ceylon, Singapore, Bombay, Madras, Burma. America: California, Mexico, Cuba, Haiti, Jamaica, Domingo, Brazil and Chile. It will be noted that the list is a comprehensive if not complete one. There is no other natural wax known that has so wide a distribution as beeswax (see Table 13). The United States imports much of its beeswax from Benguella, West Africa; from Brazil, Chile, the Caribbean countries, and other Latin American sources (also see p. 44).

The principal source of wax in the West Coast of Africa is Benguella, a province of Angola. The extent of the exports of beeswax from these Portuguese colonies is given by Lepierre and Carvalho[81] of Lisbon:

Angola	941,372	kilograms
Mozambique	151,747	
Guinea	86,836	
Timor	32,655	
	1,212,606	

The composition of the beeswax is listed by these authors as *cerotic* C_{27}, *melissic* C_{31}, *montanic* C_{29}, *neocerotic* C_{25} acids, corresponding alcohols, and the hydrocarbons C_{25}, C_{27}, and C_{31}.

Refining Crude Beeswax. Many ways have been devised to refine beeswax and lighten its color, including a number of patented processes. A preferred method is that in which the wax is melted under water with sulfuric acid (less than 5 per cent strength). The residue left after the wax extraction is known as *slumgum.* Other acids have no advantage over sulfuric acid. The addition of peroxide of hydrogen to the sulfuric acid aids the bleaching.

If the wax has already been refined it can be melted and bleached by the introduction of fuller's earth at a temperature of 153–170° and then filtering. Animal charcoal has been used in bleaching. Another method describes the use of permanganate. Bisson and Dye[16] describe a method in which the crude wax is melted in direct contact with an alkaline solution to extract the alkali-soluble impurities. The wax is then cooled and separated from the aqueous solutions, again melted, and then brought into contact with a second aqueous solution of salt and hypochlorite while stirring; when the whole is cooled, the purified product is separated.

Reichert Campbell, Hinegardner and London[115] treat the wax in the molten state with an alkaline solution of hydrogen peroxide, having the pH of the resultant emulsion between 7 and 14, and then permit the emulsified wax and alkaline solution to remain in contact without agitation for a period sufficient to bleach the wax. Zinc oxide is also used with the peroxide as a bleaching powder.

Steam extractors are commonly used for extracting beeswax; the steam, however, is not an effective bleaching agent. Steam extractors are the Ferris, Swiss, Root, etc. Purification by steam seems to have originated in France. Benzoyl peroxide has been used in bleaching such waxes after extraction.

Humes[64a] found that beeswax can be purified by distillation in the range of 0.001–0.1 mm pressure and a temperature between 180 and 230°, depending upon the pressure. The product condensed at 95° is characterized by the following constants; melting point 55–65°, acid value 40–65, ester value less than 30, and iodine number 5–10. The refined wax is white in color, practically odorless, and is said to promote the retention of emulsified water in creams, making it of particular value in the cosmetic and pharmaceutical fields.

Peroxide Method of Bleaching. Water slightly acidulated with H_2SO_4 is brought to a boil. To this is added the crude wax. The impurities settle and the refined wax is removed from the top. Then more crude is added, until the impurities become excessive. In the second step the refined wax is treated with 0.5 per cent of its weight of zinc oxide and 2.5 per cent of its weight of (100 vol.) hydrogen peroxide. The whole is agitated for 4 hours at 180° F. In the third step, water is added to the wax to the extent of four times the weight of the wax; the water has sodium peroxide added to it to the extent of 5 per cent of the weight of the wax. The whole is agitated gently and allowed to bleach over night at 180°. Then it is cooled somewhat and neutralized with dilute H_2SO_4 (1.5 pounds of H_2SO_4 for each pound of Na_2O_2). This is decanted and washed with water made acid with H_2SO_4, to neutralize and wash out any alkali and the zinc oxide. The method has a broad application to the bleaching of many waxes.

Yellow Wax—U.S.P. Quality. Genuine refined beeswax falls into two divisions, *yellow wax* and *white wax*. The United States and the British Pharmacopœias recognize both, referring to the yellow wax as *cera flava* and to the white as *cera alba*. The latter is prepared from yellow wax by exposing it to air, light, and moisture. The bleaching is often done as follows: the wax, previously melted, is made to fall in streams upon a revolving cylinder, kept constantly wet, upon which it concretes, forming thin ribbon-like layers. These are removed and spread on linen cloths stretched on frames and exposed to the air and light, care being taken to water and occasionally turn them. In a few days they are partially bleached; but to deprive the wax completely of color, it is necessary to repeat the whole process once, if not more. When sufficiently white, it is melted and cast into small circular cakes.

Yellow wax, according to the U.S.P. definition[140], is a yellowish to brownish-yellow solid having an agreeable honey-like odor, and a faint characteristic taste. The specific gravity is from 0.950 to 0.960 at 25° (77° F). The melting point ranges from 62° to 65° (143.6–149.0° F). It is somewhat brittle when cold, and when broken presents a granular, noncrystalline fracture. From the heat of the hand the wax becomes plastic. The tests for purity are fully described in the Pharmacopœia. In determining the acid and saponification values it is better to use 2 parts of benzene and 1 part of ethanol, than to use ethanol alone.[52] Five grams of the wax are dissolved in 75 ml of the mixed solvent in determining the acid value. The saponification value is determined by boiling with 75 ml of benzene and 25 ml of *N*/KOH, dissolved in ethanol.

The German Pharmacopœia specifies the acceptable limits of the acid value of beeswax as 18.7–24.3; ester value 72.9–76.7, and ratio number as 3.6–3.8. Buchner[22] questioned the values given in these limitations. Ryan[119], University of Dublin, stated that the specifications of a true beeswax, *Apis mellifica*, should be as follows: melting point 62–65°; density 0.960–0.970 at 15.5°; acid value 19–22; ester value 70–78; ratio number 3.5–3.8; iodine number about 2.12. Ryan says that adulterants, if any, may be detected by means of an uncertain melting point and high hydrocarbon content. Beeswax has a flash point of 242–250°, and 245–258° when bleached; adulterants like ceresin, japan wax, and stearic acid lower the flash point appreciably.

White Wax—U.S.P. Quality. Bleached purified beeswax, *cera alba*, as described by the U.S.P.[140] is a white shining wax, diaphanous in thin layers, inodorous, insipid, harder and less unctuous than the yellow, soft and ductile at 35° (95° F), and fusible at 65° (149° F), retaining its fluidity at lower temperature. The density is 0.959–0.975 at 15.5°; saponification value 85–107; acid value 18–22; ester value 64–80; Buchner ratio 3.4–3.9; hydroxyl number 15.0; iodine number (Hübl) 7–11; refractive index 1.447–1.465 at 65°; and melting point 61–70°.

According to the German Pharmacopœia, white wax should have an acid value 18.7–22.4; ester value 74.8–76.7, and a Buchner ratio 3.6–3.8, which Buchner[22] corrected later to 4.0–3.42. In 1936 the official French constants adopted were: density 0.960–0.966; melting point 62.5–66.0°;

Hübl ratio 3.4–3.9; saponification value 92–102; acid value 18–22; and ester value 72–80.

Chemical and Physical Constants of Beeswax. Vansell and Bisson[143] reported sixty samples of crude beeswax as having the following chemical and physical constants:

	Minimum	Maximum	Average	Pure
Acid value	16.8	35.8	19.2	17.0
Iodine number (Hanus)	6.8	16.4	10.2	5.8
Saponification value	89.3	149.0	96.7	84.4
Ash content	0.005	0.037	0.019	near 0
Melting point	62.0°	65.0°	64.0°	64.0° ± 0.9°
Solidifying point	60.7°	63.5°	62.7°	63.5° ± 0.9°
Density at 20°	——	——	——	——
Refractive index $\left(n_D^{80}\right)$	1.4388	1.4527	1.4407	1.4402

Color: yellowish-white to brown *vs* white for the pure.

The average acid value of wax collected from the "scales" of the comb was 17, whereas that for a sample of "propolis" from the side walls was 125. Contamination of beeswax with propolis is very objectionable in the manufacture of cosmetics and ruins the wax for candle making, but is not so objectionable when the wax is used for plant grafting, thread waxing, and waterproofing. The gums and pitches which constitute propolis are not secreted by the bees, but originate from numerous plant sources, especially species of poplar in the western states of the United States. The color of beeswax is affected very adversely by contact with wax during the rendering process, but nickel, aluminum, Monel metal, stainless steel, and glass vessels have little or no effect. Galvanized iron is satisfactory for solar extractors but is very objectionable for hot-water rendering. Partial clarification of the strained wax can be brought about by boiling for at least ten minutes in 5 per cent sulfuric acid. Acid treatment, followed by thorough washing, has little effect on the original acid value of the wax, but the wax appears to be slightly harder and more brittle.

Minimum and maximum values for the constants of 18 samples of beeswax from hives in different parts of Uruguay were reported by Lees and Ibarra as follows: Sp. gr. 0.9272, 0.9697; acid value 17.5, 22.4; saponification value 82.04, 105.88; ester value 63.84, 84.88; iodine number 3.36, 10.03; n_D^{70} 1.4424, 1.4442; impurities 0.86, 2.65 per cent.

The saponification values for various types of commercial beeswax have been listed by Buchner as follows:

Crude	88–106
Sun-bleached	90– 98
Chemically bleached	93–108
Pressed	81
Solvent-extracted	64–102
Crude Indian (Ghedda wax)	75–145

Specimens of pure sun-bleached beeswax from a bleachery at Babylon, New York, showed a melting point of 62.2°–63.3° and saponification value 108.7 for the "semi-bleached"; and a melting point of 66.6° and saponification value of 98.9 on the more expensive "fully bleached" grade. The so-called French standard for pure white beeswax calls for an appreciably higher melting point than that customarily assigned to yellow wax.

The freezing or solidifying point of yellow beeswax is about 60–61°, for waxes having a melting point of 63–64°. The softening point (s.p.) in water for American beeswax is 49.0–53.3° (120–128° F), which is reasonably high; and this fact makes beeswax a desirable component for wax blends that have a paraffin foundation, since it offsets the much lower softening point of the ordinary paraffins.

African beeswax, with exceptions (*e.g.,* Sudan, Gold Coast, Uganda Protectorate) has somewhat different constants from the waxes of European origin, or from those produced in America. *Kenya wax* has a density of 0.949–0.965, acid value 17.3-21.6, ester value 87.1, and ratio number 3.6 –4.2. *Tanganyika wax* is said to have a somewhat higher than normal iodine number when compared to Gambia wax. Buchner[20] gives the following constants for African beeswax: acid value 19.9; ester value 79.4; ratio number 4.0; and iodine number 11.6.

The waxes of South and East Asia (see Table 13, page 54) are distinguished from all others by a low acid value, ranging from 6.3 to 9.0, and a high ester value (78.5–96.0), the saponification value being about the same as in other waxes.

Hata[56] has shown that beeswax made by bees collecting honey from citrus trees has an entirely different composition from that of ordinary beeswax. The Formosan product contains 80 per cent of unsaponifiable substance, comprising 22.4 per cent higher alcohols, and 57.6 per cent hydrocarbons. The principal constituents are *hentriacontane* and *ceryl alcohol,* with a small amount of *melissyl alcohol, nonacosane, heptacosane* and *pentacosane.* The fat acids of the wax consist mainly of *palmitic,* with a small amount of *oleic, cerotic* and *melissic acids.*

Beeswax is soluble in ether, chloroform, and carbon tetrachloride; partially soluble in cold benzene or carbon disulfide; sparingly soluble in cold alcohol, and partially soluble in boiling alcohol, the free acids going into solution, but the esters remaining behind. Beeswax is insoluble in water, soluble in vegetable oils but not in mineral oils at ordinary temperatures. With trichloroethylene, C_2HCl_3, small quantities of the free acids and the esters and most of the hydrocarbons dissolve. The soluble part melts at 54.5° and the insoluble part at 67.3°.

Solubility of Beeswax in Various Solvents
(grams of wax per 100 grams solvent)

	at 25°	at 35°	at 45°
Ethanol (95% by vol.)	0.41	0.97	1.56
Benzene	24.2	64.2	106.8
V.M. & P. naphtha	5.0	20.0	41.0
Turpentine	8.0	26.0	59.0
Solvenol	6.0	23.0	55.0
Ethylene dichloride	1.67	4.97	20.3
Pine oil	—	5.0	27.0

The hardness of beeswax varies considerably with changes in temperature and in quality. The hardness units listed below were determined by means of a Shore durometer on (1) specimen of U.S.P. beeswax m. 61.6° purchased from Eimer & Amend, New York; (2) an ordinary dark yellow wax m. 62.3° refined from old combs; and (3) a sun-bleached wax m. 63.3° U.S.P.

Temperature	Hardness of (1)	of (2)	of (3)
−7°	—	90	—
0°	76	87	90
10°	65	80	88
20°	54	73	81
25°	47	69	76
30°	40	—	72

The hardness at 0° corresponds to a penetration test of 5 for (1).

The refractive indexes of various beeswax samples are compared below:

Refractive Index Readings at Different Temperatures of
Beeswax Samples of Known Purity[43]

Locality	At 65°	At 75°	At 85°
Mexico	1.4449	1.4414	1.4380
North Carolina	1.4453	1.4416	1.4377
Wisconsin (a)	1.4460	1.4426	1.4388
(b)	1.4443	1.4406	1.4367
Cuba	1.4441	1.4403	1.4365
Habana	1.4449	1.4412	1.4375
Haiti	1.4448	1.4410	1.4374
Southern States	1.4448	1.4414	1.4374
Africa	1.4458	1.4424	1.4387
New York	1.4456	1.4420	1.4384
San Domingo	1.4488	1.4451	1.4415
Illinois	1.4460	1.4424	1.4388
Texas	1.4449	1.4413	1.4377
Iowa (a)	1.4444	1.4405	1.4368
(b)	1.4458	1.4422	1.4384
Utah	1.4450	1.4413	1.4378
California	1.4444	1.4405	1.4368
Hilo (a)	1.4436	1.4398	1.4361
(b)	1.4434	1.4398	1.4362
(c)	1.4435	1.4400	1.4375
Minnesota	1.4470	1.4433	1.4395

Note: Samples were furnished by the Bureau of Entomology to the Contracts Laboratory, Bureau of Chemistry, Washington, D. C.

Refractive Index Reading at Different Temperatures of Commercial Samples of Proven Adulteration[43]

Contract Lab. No.	At 65°	At 75°	At 85°	Remarks
12632	1.4379	1.4340	1.4302	paraffin present
12634	1.4380	1.4344	1.4307	paraffin present
12635	1.4379	1.4342	1.4302	stearic acid and paraffin present
12636	———	1.4540	1.4505	resin present
12637	1.4375	1.4338	1.4301	paraffin present
12638	1.4350	1.4313	1.4275	paraffin present
12641	1.4421	1.4384	1.4346	paraffin present
12642	1.4363	1.4323	1.4284	paraffin present
12648	1.4421	1.4384	1.4348	paraffin present
12649	1.4335	1.4300	1.4260	stearic acid and paraffin present
12655	1.4441	1.4406	1.4369	pure wax
12630	1.4463	1.4425	1.4389	pure wax

NOTE: Upon examining data it will be found that the refractive index at 75° for pure beeswax falls between 1.4398 and 1.4451.

Chemical Composition of Beeswax. For the past century the chemical composition of beeswax has been a subject of discussion, and has been revised repeatedly as a result of improved methods in the technique of identification of the constituents in waxes.

As early as 1814 an attempt was made to analyze beeswax for its chemical components. The wax was treated with boiling alcohol; the insoluble portion was given the name *myricin*, and the portion which dissolved, but crystallized out on cooling, was designated *cerotic acid* (m. 67°). In 1848 Brodie identified myricin (m. 64.5°) as consisting principally of an ester of palmitic acid, which he called *myricyl palmitate* (m. 73°). It was later shown by others that myricin contains hydrocarbons as well as esters. The portion which remained dissolved in the cold alcoholic liquid was called *cerolein* (m. 53.5°) which however was later shown to be a complex containing unsaturated compounds. Schwalb in 1886 discovered melissic acid in beeswax, and also fat acids of lower molecular weight, such as palmitic and hypogaic.

It is generally conceded that the principal constituent of beeswax is *myricyl palmitate*, $C_{15}H_{31}CO \cdot O \cdot C_{30}H_{61}$. Marie assigned the formula $C_{25}H_{50}O_2$ to the free *cerotic acid* in beeswax, but at least a large portion of this acid is regarded now as $C_{26}H_{52}O_2$. In 1893 Marie also assigned the formula $C_{30}H_{60}O_2$ to *melissic acid*, which Damoy in 1924 showed to be $C_{31}H_{62}O_2$.

The presence of a C_{30} acid in the saponified acids has been more recently proved by molecular vacuum distillation. The C_{30} acid should be properly called *myricinic acid*, as it is an oxidation product of *myricyl alcohol*. Brodie was the discoverer of myricyl alcohol, to which he gave the formula $C_{30}H_{60}O$. Gascard[48] disputed the formula and assigned it $C_{31}H_{64}O$, now known as melissyl alcohol. Through an extensive analytical investigation Gascard was able to position *melissyl melissate* (m. 90.5°) and *myricyl laccerate* (m. 95°) in the series of esters. Gascard obtained the hydrocarbon $C_{31}H_{64}$ (m. 69°) by reducing the iodide of the alcohol.

Gascard described *melissyl alcohol* as a C_{31} alcohol that consists of tiny white lozenges when crystallized from benzene, and stated that it is a normal alcohol (m. 87°) and a homolog just below *lacceryl alcohol* (m. 89°) which he had isolated from commercial stick-lac. It would seem quite possible that the C_{31} alcohol is a mixed dimer of C_{30} myricyl and C_{32} lacceryl alcohols. *n-Melissyl margarate* has been considered as a constituent of beeswax.

Damoy[33] in 1924 recognized C_{25}, C_{27}, C_{29} and C_{31} wax acids in beeswax. By fractional precipitation with magnesium acetate and micro-fractional distillation in high vacuum Holde and Bleyberg were able to obtain the C_{25} to C_{31} acids referred to by Damoy. Ikuta reported the presence of *hexacosanic acid* ($C_{26}H_{52}O_2$), cerotic (*b*) and *hydroxy-palmitic acid* (probably oxyhypogaic, or oxypalmitoleic acid) in Japanese beeswax.

The melting points of the acid, alcohol, and hydrocarbon components of beeswax have been determined by Gascard[49] as: *neocerotic acid* 77.8°; *pseudocerotic* (C_{27} acid) 82.5°; *montanic acid* 80.0°; *melissic acid* 90.0°; *neoceryl alcohol* 75.6°; *ceryl alcohol* 80.0°; *montanyl alcohol* 84.0°; *myricyl alcohol* 87.0°; *pentacosane* 54–54.5°; *heptacosane* 59.2–59.5°; *nonacosane* 63.5°; *hentriacontane* 68.4–69.0°.

Psyllic acid ($C_{32}H_{64}O_2$) is a methyl side-chain acid which has been identified with the propolis of the honeycomb. Kebler[68] in 1893 estimated the hydrocarbon content of beeswax as 12.7 to 14.8 per cent. Leys[84] (Paris) in 1913 found 10.4 to 13.0 per cent hydrocarbons. Leys reported 39.2–39.6 per cent alcohols (m. 77–80°, acetates m. 54–57°) in the saponified beeswax. He assigned the iodine numbers 13.8–15.6 to the hydrocarbons. The only unsaturated hydrocarbon reported in connection with beeswax is melene ($C_{30}H_{60}$), an olefin which is obtained by pyrolysis of beeswax, and the constitution of which was first determined by Marcusson and Böttger;[92] it is not a constituent of beeswax. It is not unlikely that the iodine number of Leys was that of cholesterol or cholesteryl ester, if this was not completely saponified in the analysis.

In the light of our present knowledge, it appears that in the metamorphosis of wax by the bee a whole series of alcohols, with an even number of carbons, is initially produced by a systemic coupling of hydroxylene radicals into dimeric groupings and the coupling of such groupings, these reactions taking place with the elimination of moles of water and the linkages aided by free hydrogen. These alcohols range from C_{14} to C_{32}, but soon become oxidized by free oxygen to the corresponding C_{14} to C_{32} acid moles. However, the more immobile or highest alcohols combine with the lower acids of the series in preference to directly reacting with oxygen; as a result esters are formed between the C_{30} and C_{32} alcohols with the C_{14} to C_{22} acids. The chief acid of the C_{14} to C_{22} group is *palmitic acid*; and since the chief alcohol of the C_{30} to C_{32} group is *myricyl alcohol*, the union of these produces a large amount of *myricyl palmitate*. The small amount of *myristic acid* forms a lactone, namely *ω-myristo-lactone* (m. 41–42°). Acids are formed in excess in the range of C_{24} to C_{34}, the principal one of which is the C_{26} acid, *cerotic* (*b*) or 1-hexacosanic (m. 87.8°).

However, most of the C_{26} acid mole combines with C_{24} to C_{30} moles to form bimolecular compounds, also known as mixed dimers, resulting in a series of acids with an odd number of carbons; these are to be found in crude cerotic acid, soluble in hot ethanol but insoluble in cold, in the alcoholic extraction of beeswax. These dimers are C_{25} acid, *cerotic* (*a*) (m. 78°) which has been referred to as *hyaenic acid*; C_{26}, acid, *cerotic* (*b*) (m. 87.8°); C_{27} acid, *cerotic* (*c*) (m. 82.5°); C_{29} acid, *montanic* (m. 86.8°); and C_{31} acid, *melissic* (m. 90°).

These acids can be separated only as "even carbon" acids through esterification to the monomeric esters, and fractionation of the latter. Beeswax contains hydrocarbons with an odd number of carbons which are end residues resulting from decarboxylation of the esters in the metamorphosis, more particularly hentriacontane ($C_{31}H_{64}$) produced by the decarboxylation of palmityl palmitate (cetyl palmitate) as it is formed.

Chemical Composition of Yellow Beewax
(alcohols 60; acids 42.5 parts)

Alkyl Esters of Fat and Wax Acids: 72 per cent
(Combining wt. 700, m.p. 63.5°)

$C_{15}H_{31}CO \cdot O \cdot C_{30}H_{61}$	myricyl palmitate (33%)
$C_{15}H_{31}CO \cdot O \cdot C_{32}H_{65}$	lacceryl palmitate (9%)
$C_{15}H_{29}CO \cdot O \cdot C_{30}H_{61}$	myricyl palmitoleate, m. 38° (12%)
$C_{15}H_{28}(OH) \cdot CO \cdot O \cdot C_{30}H_{61}$	myricyl hydroxypalmitate (6%)
$C_{25}H_{51}CO \cdot O \cdot C_{30}H_{61}$	myricyl cerotate (12%)

Cholesteryl Esters of Fatty Acids: 0.8 per cent
cholesteryl palmitoleate, m. 40°

Lactones: 0.6 per cent
ω-myristo-lactone, m. 41–42°

Free Wax Acids: 13-13.5 per cent.
(Combining wt. 376.8, m.p. 77.5-79°)

$C_{25}H_{50}O_2$	neocerotic acid, m. 77.8° (Gascard)
$C_{27}H_{54}O_2$	cerotic acid (*c*), m. 82.5° (Brodie)
$C_{29}H_{58}O_2$	montanic acid, m. 86.8° (Holde)
$C_{31}H_{62}O_2$	melissic acid, m. 90° (Damoy)

Hydrocarbons: 12-12.5 per cent

$C_{19}H_{40}$	nonacosane, m. 63.5° (G)
$C_{21}H_{44}$	hentriacontane, m. 68.7° (G) (11%)

Moisture: 1-2 per cent

Ghedda Wax

Singh reports that three species of honeybees are found in Punjab, which are suited to different climatic conditions. The Indian bee, *Apis indica*, F., is found in the hilly tracts; the little bee, *Apis florea*, F., in the plains where in summer the temperature may rise to 120° F or so; and the giant bee, *Apis dorsata* F., remains in the sub-mountainous tracts and lower hills and has not been found in the higher mountains. Chinese bees are believed to be a variety of *Apis indica*, known as *Apis peroni*, and produce a very white wax.

The introduction of the artificial comb made of a paraffin composition material for use in beehives led to an acute shortage of domestic wax in Germany in 1905, and as a result foreign beeswax became a dominant factor in the German market. It became necessary then to recognize normal variations in the composition of the waxes imported from East Africa, British India, East Asia, and South America. Berg[12] found that waxes originating in South and East Asia may be distinguished from all others by a low acid number and a high ester number. Buchner had referred to the simple ratio of the ester number to the acid number as an important analytical constant, which became known as the "Buchner number," according to Berg, or simply as the "ratio number."

East Indian beeswax became later known as *Ghedda wax*, or *gedda wax*, and is defined as a wax produced by a bee other than the common honey bee, *Apis mellifica*. Buchner in 1905 conducted an extensive investigation into the species of bees that produced the beeswax imported into Germany, and found that there were a number of species of bees which he enumerated as *A. dorsata*, *A. florea*, *A. indica*, *A. fascista*, and *A. sinensis*. In his report to the *Chemiker-Zeitung* in 1906 he says that the *A. dorsata* is the largest bee, and the *A. florea* the smallest. He regarded *A. indica* or *A. fascista* as really varieties of *A. mellifica*, and stated that *A. dorsata* is a bee which builds a giant genuine two-sided comb. We now know the *A. indica* is a very distinct species, although of common size. The data on analytical constants given by Buchner are classic and instructive.

Source		M. P. (°C)	Acid No.	Sapn. No.	Iodine No.
Apis dorsata (23 samples)	mean	63.1	7.0	96.2	6.7
	max.	67.0	10.2	105.0	9.9
	min.	60.0	4.4	75.6	4.8
Apis florea (5 samples)	mean	64.2	7.5	103.2	8.0
	max.	68.0	8.9	130.5	11.4
	min.	63.0	6.1	88.5	6.6
Apis indica (7 samples)	mean	63.25	6.8	96.2	7.4
	max.	64.0	8.8	102.5	9.2
	min.	62.0	5.0	90.0	5.3
Apis mellifica	mean	63.25	20.0	95.0	7.5
	max.	65.0	21.0	99.0	11.0
	min.	61.5	17.5	87.5	4.0

The analyses of Ghedda wax, *A. indica* type, indigenous to various Asiatic countries have been reported as follows.

Country	Sp. Gr. 15°	M. P. (°C)	Sapn. Value	Acid Value	Ratio No.	Iodine Value
Assam (N. E. India)	0.965	61.0	97.8	5.8	16.7	5.6
Annam (Fr. Indo-China)	0.964	61.0	86.6	7.8	10.4	6.0
China	——	62.5	108.6	7.5	13.0	——
Eastern Bengal	0.973	66.4	103.2	7.6	12.2	7.7
Japan	0.——	65.7	94.8	6.9	13.2	12.6
Korea (*A. indica*)	0.——	65.6	84.5	5.8	13.4	11.4
Philippines	0.961	63.2	101.6	6.9	14.0	9.1
Macassar (Batavia)	0.956	60.5	118.8	7.0	12.0	6.6

Ghedda wax is indigenous to British India, Siam, Annam, Cambodia, Tonkin, Batavia, Korea, Japan and the Philippines. The wax is generally exported from Bengal, Bombay, Madras, Burma, Shanghai, and Sind to the English market. A composite sample of wax of the secretions of *A. dorsata*, *A. florea*, and *A. indica*, with very little wax of *Trigona* species was reported by Ragaswami (Madras, India) in 1941, as having a sp. gr. at 15° of 0.963, m.p. 63.0°, sapn. value 94.0, acid value 6.1, ester value 87.9, iodine value 5.8.

Ghedda wax is pale to dark-yellow in color, quite firm in consistency, but of a fatty feel. When genuine beeswax is adulterated with Ghedda wax it is said to be difficult to detect the adulteration except through chemical analysis in which the constants for acid, saponification, and iodine evaluations are determined. The specific gravity of Ghedda wax is 0.956 –0.973 at 15°. The refractive index at 80° is 1.4404 or thereabouts. Ghedda wax melts at 60.4–66.4°, the limits being wider than those of beeswax (63–64°). The solidification point of Ghedda wax is about 60°. The saponification value ranges from 86 to 130, acid value 3.5 to 10.5, ester value 69 to 123, and iodine number (Hübl) from 4.8 to 11.4. The ratio number (ratio of acid to ester value) limits set by Berg were 1 : 9.9 to 14.9 for Ghedda wax, contrasted with 1 : 2.9 to 4.5 for genuine beeswax.

Chemical Composition of Ghedda Wax. The chemical composition of Ghedda wax differs from that of beeswax in many respects. The transition of pollen principles to wax by the bee seems to lie in the conversion of tripalmitin and tripalmitolein (glycerides existing as plant principles) into monohydric alcohols which recombine with an excess of the free acids formed. The hydrocarbons are simply end products of metabolism, and the glycerol liberated is consumed as a food. Any cholesterol produced would be in the form of an ester of the fatty acid. The transition of plant principles to wax differs somewhat for the East Indian bees. The conversion appears to be from principles like trimyristin and trimargarin (or the mixed glyceride of palmitic and stearic acids) into corresponding free acids and alkyl esters.

As previously mentioned, in beeswax there appears to be an appreciable amount of unsaturated hydrocarbon known as melene, produced in melting the wax. In Ghedda wax unsaturated hydrocarbons are absent, which accounts for the low iodine numbers. Refined beeswax is free from fattiness and contains no glycerides. Ghedda wax is quite fatty and contains a proportion of highly saponifiable matter which has not yet been positively identified, but is calculated as myristin, and is probably the metabolic source of the *ceryl alcohol* in the composition of the wax. Stearin plays a metabolic role in the formation of *geddic acid* in Ghedda wax; stearin appears to be absent as a factor in the metabolism of beeswax. We might expect to find a small amount of the ester, *lacceryl ceromelissate,* in Ghedda wax, for the same reason that we find *ceryl cerotate* in beeswax. The presence of higher hydrocarbons in Ghedda wax might be expected because of the source of higher glycerides in the plant principles. The presence of hydroxymargaric acid in Ghedda wax is also explainable on the basis of carboxylation by the insect of palmitoleyl alcohol. The role of metabolism is still speculative.

Lipp and Kuhn[87], of Munich, in 1913 determined the chemical composition of Ghedda wax. They saponified the wax with 0.5N alcoholic potassium hydroxide for 8 hours, neutralized the solution with 0.5N hydrochloric acid, evaporated the solution and extracted the residue with petroleum ether. For identification the extract was dried and heated with soda lime and converted into cerotic acid, from which the following derivatives were made: methyl ester (m. 60°), lustrous plates; acid amide, fine needles (m. 106°, Marie 109°); anilide, fine white needles from alcohol (m. 53.5°). The wax also yielded two hydrocarbons, $C_{26}H_{54}$ and $C_{30}H_{62}$ (m. 58° and 70° respectively), but Lipp and Kovàcs[88] later showed each of the hydrocarbons to be at least one homolog higher, namely $C_{27}H_{56}$ and $C_{31}H_{64}$. Ghedda wax contains *ceryl alcohol* to the extent of 48 per cent in combination with margaric (or palmitic-stearic complex) according to Buchner, whereas genuine beeswax contains the higher alcohol, myricyl. The esters of Ghedda wax contain 58.8 parts of alcohols to 44.0 parts of acids.

Lipp and Casimer[86] have reported the percentage of Ghedda wax constituents which they determined: ceryl alcohol 48, heptocosane 5, hentriacontane 2, hydroxymargaric acid 24–25, an isomeric hydroxymargaric acid 1.5–2, margaric acid 9–10, palmitic acid 8–9, geddic acid 2, cerotic acid 1, traces of formic, ethyl and propyl alcohols, and resin.

Lipp and Casimer[86] have determined the chemical composition of a Ghedda wax having the following constants: m.p. 62–3°, acid value 6.1–5.8, ester value 91.5–90.8. The only alcohol which they could find in the unsaponifiable was *ceryl alcohol* (m. 74°). (This corresponds to the C_{24},C_{26}

dimer). They reported the methyl ester (m. 60°), acid amide (m. 106°, Marie 109°), and ceryl benzoate (m. 53.5°). (The ester corresponds to C_{25} ester). The acids combined with the ceryl alcohol are *hydromargaric acid* (m. 58°), an isomer of same (m. 71–72°), *palmitic,* and *stearic.* The free acids are described as *cerotic* and *geddic.* The latter crystallizes from ethyl acetate in a mossy aggregate of needles, 94.5–95°. Geddic acid is insoluble in ether. The authors state that geddic acid is not to be confused with the melissic acid of genuine beeswax, since it has the formula $C_{34}H_{68}O_2$. They also isolated two hydrocarbons, heptacosane and hentriacontane. The composition of Ghedda wax appears to be approximately as follows:

Alkyl Esters of Fatty Acids: 87 per cent
(m.wt. 663)

ceryl myristate, m. 59°
ceryl palmitate, m. 69° (20%)
ceryl stearate, m. 73°
ceryl hydroxymargarate (4%)
melissyl margarate, m. 79°

Free Fatty Acids: 5 per cent
(m.w., 391, neutr. no. 143)
cerotic acid, m. 76–77° (1%)
geddic acid, m. 95° (2%)
margaric acid, m. 61.3° (2%)

Hydrocarbons: 7 per cent
heptacosane, m. 59–59.5° (L&K) (5%)
hentriacontane, m. 68–68.5 (L&K) (1%)
tritriacontane, m. 71.8° (1%)

Japanese beeswax is not identical with East Indian wax, nor is it the same as genuine beeswax. According to Ikuta, Japanese beeswax has 4–6 per cent of free acids, and 38–41 per cent of combined fatty acids. Of the mixed fatty acids about 20 per cent is reported to be hydroxypalmitic acid (m. 73.8–74.2°).

Uses of Ghedda Wax. The uses of Ghedda wax have been almost as wide as those for genuine beeswax and considerable tonnages are exported each year to Russia, Germany and Great Britain. It is reported in India that the wax is used for candle-making, and that it makes a suitable foundation for ointments and plasters. The yellow color is to a large extent removable by activated carbon or by kieselguhr. Considerable quantities of the Macassar beeswax are said to have been used by the American manufacturers of sound records prior to World War II. This wax has an ivory color, is quite fatty, and does not possess the distinctly fragrant odor of beeswax. The Chinese, Korean, and Japanese wax is credited with being of better quality than the Indian, since it is harder, cleaner, and of better color.

Table 13. Summary of Properties of Beeswax

Habitat	Species Indicated	Melting Point (°C)	Specific Gravity at T°C	Saponification Value	Acid Value	Ester Value	Ratio Number	Iodine Value	Clouding Point (°C)	Reference
United States	*A. mellifica*	64.0	0.963/15	96.7	19.2	77.5	4.0	10.2	60.5	Vansell & Bisson
Canada	*A. mellifica*	64.2	0.964/15	89.4	18.0	71.9	4.0	10.0	60.0	Baril, *C.A.* **28**, 6008 (1934)
Cuba	*A. mellifica*	63.7	0.961*	95.2*	18.0	75.0	4.2	10.2*	60.0	Salamon
Brazil	*A. mellifica*	65.5	0.962	96.2	19.0	77.5	4.1	9.2	—	Berg
Chile	*A. mellifica*	64.5	0.965	90.0*	18.5	72.3	3.9	—	60.0	Salamon
Argentine	*A. mellifica*	64.0	—	97.0*	19.6	73.5	3.8	—	—	Berg
Australia	*A. mellifica*	64.2	—	95.7	19.0	76.0	4.0	9.5	—	Berg
San Domingo	*A. mellifica*	63.5	0.962*	93.5	18.5	72.0	3.9	—	60.0	Salamon
Portugal	*A. mellifica*	64.0	0.966*	91.8*	18.4	72.0	3.9	10.7	60.0	Salamon
Germany	*A. mellifica*	64.0	0.961	94.5	19.6	72.5	3.7	7.7	—	Berg
Gold Coast	?	64.5	0.829/99	90.8	20.5	70.3	3.4	—	—	Anon.
Greece	*A. mellifica*	64.5	0.962	93.9	18.6	75.3	4.0	8.8	—	Emmanuel
Poland	*A. mellifica*	63.5	—	96.8	19.3	77.2	4.0	6.7	—	Berg
Sweden	*A. mellifica*	63.5	—	96.8	20.1	76.0	3.8	9.3	—	Berg
Spain	*A. mellifica*	64.0	—	96.0	18.2	75.0	4.0	11.0*	60.0	Salamon
Italy	*A. mellifica*	63.5	0.964/15	94.1	19.9	74.5	3.8	9.1	60.5	Cortese, *C.A.* **22**, 2283 (1928)
Ireland	*A. mellifica*	64.5	—	—	20.0	76.0	3.8	6.0	—	Ryan, **8**, 2272
Abyssinia	*A. adansonii*	63.5	0.958*	94.0	19.8	74.5	3.8	—	—	Salamon, *J.S. Chem. Ind.*, **35**, 8–10 (1916)
Egypt	*A. facista*	63.4	—	97.1	19.4	74.0	4.0	8.0	59.8	Berg
Morocco	*A. adansonii*	63.5	—	—	19.0	76.0	4.0	—	60.0	Salamon
East Africa	*A. scutela*	63.0	0.957	93.3*	18.5	75.0	4.0	—	—	Salamon
Madagascar	*A. unicolor*	64.0	0.960*	98.0*	18.5	75.0	4.0	—	60.5	Salamon
Mozambique	*A. adansonii*	63.5	0.958*	94.9	18.5	75.0	4.0	—	60.0	Salamon
South Africa	*A. adansonii*	63.5	—	—	19.1	79.4	4.1	11.6	—	Buchner, *C.A.*, **14**, 854
Sierra Leone	*A. adansonii*	64.0	—	—	19.0	75.0	4.0	—	60.0	Salamon
Northern Nigeria	*A. adansonii*	63.7	—	93.8*	17.8	76.8	4.2*	7.7	—	Bull. Imp. Inst. C.A.G. 1547
Smyrna	*A. mellifica*	—	—	—	19.0	74.0	3.9	—	64.5	Salamon
Bengal	*A. dorsata*	63.1	0.965	96.2	7.0	89.2	12.8	4.5	56.0	Roberts & Islip, *C.A.*, **16**, 3007
Eastern Bengal	*A. indica*	64.2	0.965	96.2	6.8	89.4	13.1	7.7	56.0	Roberts & Islip, *C.A.*, **16**, 3007
Assam (India)	*A. florea*	63.2	0.965	103.2	7.5	95.7	12.8	5.6	56.0	Roberts & Islip, *C.A.*, **16**, 3007
Japan	*A. indica*	65.7	0.810*/100	94.8	6.9	90.0	13.2	12.6	—	Sokichi
Annam (Indo-China)	*A. indica*, Var. *peroni*	61.0	0.964	86.6	7.8	78.8	10.1	6.0	—	Bellier *C.A.*, **1**, 360
Korea	*A. indica*	65.6	0.823/100	84.6	5.8	78.7	13.4	11.4	—	Ueno, *Analyst*, **40**, 343–4 (1915)
Philippines	*A. indica*	63.2	0.961/15	101.6	6.9	95.0	14.0	9.1	59.0	Brill, *C.A.*, **10**, 3171
S. & E. Asia	*A. indica*	—	—	100.3	7.6	92.5	12.4	9.5	—	Berg, *C.A.*, **1**, 2021

*Determinations by other than source quoted.

Wax of Wild Bee Brood-Comb

The composition of the cellular structure of the wild bee brood-comb differs from that of the ordinary honeycomb prepared in a beehive by the bees for storing their excess honey. This difference has been shown by Warth and Hanzely[148] by an analysis of a brood-comb obtained from a bee-tree at Millvale, Pennsylvania compared with that of a honeycomb from the same state. The yield of wax materials, namely beeswax and propolis, from the cleaned bee brood-comb was 39 per cent, whereas the yield from the beehive honeycomb was more than 95 per cent. After freeing the living quarters of honey, brood, pollen, and other waste materials including leafy matter, the cleaned cells of the comb structure yielded, after wax and propolic extraction, horny shells of sclero-albumenoid, and no cellulose. The nature of the pure wax separated from both types of combs was substantially the same, but the wax extracted by solvent (chloroform) from the brood-comb shows considerably more vegetable wax constituents, which have not been wholly converted to the end stage. The average cell of a brood-comb weighs 0.1126 gram, and is larger than that of a honeycomb.

The wax materials of the brood-comb were divided into three parts: (1) *beeswax* extracted by hot water; (2) *extraction wax* removed from comb by choloroform, after freeing the pure beeswax by hot water; (3) *propolis* extracted from sludge settling from the water extraction, due to its greater density.

Chemical constants for these fractions were determined:

	Acid Value	Sapn. Value	Ester Value	Iodine No.
(1) Pure Beeswax (32.1 g)	18.1	97.5	79.4	11.8
(2) Extraction Wax (5.55 g)	27.4	130.4	103.0	33.1
(3) Propolis (1.35 g)	28.5*	174.0	145.5	52.2

*The low figure for the acid value might be due to the neglect to acidify by sulfuric acid to free the resin from tannin in its preparation. We would expect this value to be at least 77. Propolis in its free state is always decidedly acid.

The propolis of the wild bee brood-comb or that which fastens the honeycomb to the side walls of the box, as the case may be, consists of gum resin and balsam pitch, referred to as "propolis resin" and "propolis balsam," respectively. The propolis of the wild bee comb melts at 62°, but at a higher temperature if remelted. That of the honeycomb melts at 80–90°, but at 130° when preheated at 101°. The latter has the fragrance of gum benzoin, and that of the wild bee comb a faintly conifer-like odor.

The extraction wax of the wild bee comb was dark brown in color. Repeated extractions at a low temperature removed a greasy substance of acid value 91.4 and saponification value 239.1. Its removal lowered the acid value of the extraction wax to 22.9. The chemical constants of the vegetable wax portion of the comb are acid value 7, saponification value 205, iodine number 55. These constants indicate the presence of a fairly large amount of unsaturated principles, such as *palmitolein.*

A comparison of the composition of the bee tree-comb and that of the hive honeycomb is shown below.

	Bee tree-comb %	Honeycomb %
Extraction wax:		
Propolis	10	10
Vegetable wax	25	8
Beeswax	65	82
Propolis:		
Propolis resin	92.7	91.5
Propolis balsam	7.3	8.5

Propolis, as gathered from hives, has been reported as a mixture of about 70 per cent of resin melting between 90° and 100°, 10 per cent of resin melting between 60° and 70°, and beeswax 30 per cent. Propolis is usually referred to as the "varnish" with which the bees coat the cells and cappings that have stood in the hive for a protracted period.

Analysis of Bee Glue (Propolis)
(*compiled from various sources*)

	Heiduschka (%)	Dieterich (%)	Bohrisch (%)	Rabinovich (%)	Average (%)
Resin*	70.7	64.6	43.6	68.9†	61.9
Balsam	5.0	3–8	8.7	4.0	5.8
Wax	14.8	16.0	27.9	19.3	19.5
Volatile	4.2	6.0	6.9	3.5	5.1
Non-Volatile Impurities	5.3	—	12.9	4.3	7.5

*Treatment with 95 per cent alcohol extracts *propolis resin,* leaving *propolis wax* as residue. *Propolis balsam* is obtained from the resin by extraction with boiling petroleum ether.

† Crude Resin: 86.2 per cent resin, 11.4 per cent tannins, 1.8 per cent proporesin, traces of α-proporesin, 0.6 per cent β-proporesin.

Propolis Resin:	melting point 67°, (after heat treatment at 101°) 90–106°		
	specific gravity	1.186	
	acid value	114–125	ave. 119
	saponification value	about 184	
	ester value	65–70	
	iodine number	55?	
Propolis Balsam:	melting point	syrupy liquid	
	acid value	75–112	ave. 93.5
	saponification value	167.9–173.8	ave. 170.4
	ester value	61.8–93.0	ave. 77.4
	iodine number	8?	
Propolis Wax:	melting point	61–66°	ave. 63.2°
	acid value	28.4–29.0	ave. 28.7
	saponification value	97.1–97.6	ave. 97.3
	ester value	about 68.6	
	iodine number	about 20	

Pure Beeswax:	melting point	64.7°		
	acid value	18.4-18.5		
	saponification value	92.1-97.1	ave.	94.6
	ester value	73.6-79.4	ave.	76.5
	iodine number	about 10.2		

The resin is soluble in alcohol and insoluble in hot petroleum ether.

The balsam is soluble in petroleum ether and in 70 per cent alcohol.

The propolis wax is largely a vegetable wax of fairly constant composition.

The volatile matter includes 2-3 per cent of water.

The non-volatile impurities include pollen grains, meal, dust, fiber, etc., insoluble in petroleum ether and in alcohol.

The color consists of several yellow pigments, including 1-3 dihydroxy flavone, or chrysin which follows along with the petroleum ether extractions.

The composition of propolis on a water, oil, impurities-free basis is as follows:

resin	71.0 per cent
balsam	6.6 per cent
wax	22.4 per cent

Stingless Bee Wax

This is the wax produced by a wild bee sometimes referred to as the dammar bee, *Melipona* or *Trigona* species. The *Apis* was not introduced into America prior to the 17th century; the producers of wild honey and wax in pre-Columbian America were the stingless bees, the favored species of which were domesticated in Mexico, Central America, and northern parts of South America. The larger stingless bees are usually of the genus *Melipona*, and the dwarf ones of the genus *Trigona*, both belonging to family *Meliponidae*. One of the larger species is the *Melipona beecheii*, or royal bee, and it is favored for apiculture in Mexico and the Central American countries. A race of it also occurs in Cuba and Jamaica. The wax is commercially gathered in India, Trinidad, and Brazil.

According to Schwarz[123], other materials in addition to wax constitute the building blocks of *Melipona* and *Trigona*, *i.e.*, resinous substances, earth and clay, excrement, plant particles and plant exudates, tar, grease, oil, varnish, bits of wood, and doubtless other things. Foraging for these is the function of the worker bee, and upon her rests the responsibility, too, of keeping the larder supplied. The nests are usually built in the hollow trunks of trees, faces of rock, or even on the ground.

The giant *Melipona fulvipensis* constructs successive, horizontally placed combs of closely fitted brood-cells, one cell contiguous to another and on the same level. According to Schwarz, the dwarf stingless bee known as *Trigona duckei* does not arrange its brood-cells in combs, but in clusters with tiny pillars of wax connecting the otherwise independent cells; but the vast majority of *Trigona* build their brood-cells in combs as do the species belonging to the genus *Melipona*. The Kota bees [139] of India are of the latter genus. They are minute, stingless insects which furnish a sticky, dark-colored wax, resembling in physical and chemical characteristics the propolis of the honey bee. Buchner[21] records that 170 varieties of the *Meliponidae* exist. In general, the wax is described as brownish-yellow to a blackish-brown in color and of sticky consistency.

A stingless bee wax imported from Brazil into the United States, a wax of the *Melipona* species, is dark brown, soft, and of a slightly tobacco-like odor. Some of the extractables by alcohol and by acetone, however, have a fragrant odor suggestive of pure beeswax. The Brazilian wild bee wax has an acid value of 15.4, and a sponification value of 108.8 for the wax in its crude state. The crude wax, however, is about 30 per cent non-extractable, this matter consisting of earthy, vegetable, and inert substances. The purified wax is of a yellowish-brown color.

The chemical literature briefly refers to a *Trigona* wax of Trinidad which shows so wide a variation in constants that it is difficult to set up specifications for an approved quality. It is said that in general this wax is high in iodine number. Stingless bee wax from India has an acid value of 16 to 23, a saponification value 74 to 130, iodine number 30 to 50, and melting point 66 to 76°.

Stingless bee wax, like beeswax, contains *myricyl palmitate*, and a considerable amount of *cerotic acid* which can be readily crystallized from its solution in alcohol. Aside from this it contains a yellow dye, resins, hydrocarbons, and other substances which have not been clearly identified.

The following chemical composition of wild bee wax is based upon a wax with acid value 16, saponification value 72, ester value 56, iodine number 30, and unsaponifiable 60.5 per cent.

Alkyl Esters of Monobasic Acids: 35 per cent
myricyl palmitate
ceryl hydroxymargarate
myricyl cerotate

Saponifiable Sticky Resinous Matter: 14 per cent

Free Fatty Acids: 12.3 per cent
cerotic
myricinic
unidentified unsaturated

Hydrocarbons: 7.3 per cent
hentriacontane
unidentified

Cellulosic, Sclero-protein, and Mineral Matter: 31.5 per cent

Hanzely[148] extracted wild bee wax obtained from Brazil, first with ethanol, then with benzene, and lastly with acetone, using a Soxhlet extractor. The ethanol-extractable amounted to 40.6 per cent; the ethanol-insoluble but benzene-extractable 7.3 per cent; and the ethanol- and benzene-insoluble but acetone-extractable amounted to 21.2 per cent. The melting points on these extractable components were 74.5°, 76.2°, and 71.8°, respectively. When the ethanol-extractable was cooled, 34.5 per cent (of the original wax) crystallized out, and when recrystallized showed a melting point of 78.5°. The uncrystallizable but ethanol-soluble portion consisted of a sticky, amber-colored material (m. 74.5°) to the extent of 6.1 per cent. After these selective solvent extractions, the residue resembled a silt, and consisted largely of bee glue, mineral matter, and particles of leafy material. The residue amounted to 31.5 per cent.

Beeswax Adulterated with Stingless Bee Wax. According to some reports, a considerable amount of blending of waxes is done by unscrupulous vendors in commercial centers, in which Caribbean waxes of the *Trigona* species are blended with East Indian waxes when they are available, with artificial comb material, or even with a petroleum wax. The adulterated waxes vary from pale yellow to a dark brown color. The odor is generally deficient, and occasionally the characteristic odor of beeswax can be barely detected upon melting the wax. A determination of the chemical and physical constants of the sample soon determines whether the wax is adulterated, or whether it is simply deficient in quality.

During World War II many of these adulterated waxes appeared on the market as pure, refined yellow beeswax. Samples taken from one shipment of a New York supplier showed the following constants: m.p. 58.5°, acid value 20.5–21.1, saponification value 98.0–101.9, ester value 77.0–81.4, iodine number 37.3–44.8. The wax was of a dark yellow-brown color, and of a disagreeable odor.

Another adulterated beeswax offered in the New York market contained about 30 per cent of *Trigona* wax and 70 per cent of East Indian wax. The wax was of a dirty brown color, with following constants: m.p. 59°, acid value 9.7–10.0, saponification value 94.3–102.5, ester value 84.3–92.8, ratio number 1 : 8.45 to 9.60, iodine number 22.7 to 23.1.

Stingless bee is used to some extent in the shoe trade, but its greatest use seems to be in adultering Ghedda wax to bring up the melting point and iodine value to that of genuine beeswax, detection being difficult in the dark yellow grades of beeswax used for technical purposes.

Humble Bee Wax

The humble bee is of the order *Bombus*. There are two species, *Bombus terrestris*, which builds round nests of carded moss, and *Bombus lapidarius*, which makes its home in cavities among stones. The wax is so small in quantity that it is only of academic interest. Sundwik[131] described the wax which was obtained from a giant nest of *Bombus terrestris* as of interest because of its content of *psyllyl alcohol* and absence of myricyl alcohol, cerotic acid and palmitic acid, all of which are constituents of true beeswax, produced by the honey-bee *Apis mellifica*. Sundwik at Helsingfors also isolated an alcohol corresponding to the C_{34} acid which he named *incarnatyl alcohol*, and found its melting point to be 72–74°.

Ullmann's German Encyclopœdia[136] refers to humble bee wax as "Hummelwachs", and gives the following characteristics: Sp. gr. 0.960–0.969; m.p. 68–72°; acid value 18.0–19.4; saponification value 93–98.1; iodine number 5.0–7.0; and unsaponifiable 52–63 per cent.

The occurrence of wax in the lumen of the chitin hairs of *B. terrestris* has been reported by Schmidt.[122] The wax is extractable by chloroform and possesses a powerful double refraction which disappears on warming and returns on cooling. The dried hairs, however, gradually lose their double refractive power if mounted in balsam.

World Trade in Beeswax and Its Uses

The world trade in beeswax is extensive. In the United States the most important market for beeswax is in Pittsburgh, Pennsylvania. Much of the beeswax produced in the West is shipped East, the Eastern industries being the larger consumers; 3,380,000 pounds of beeswax were produced in the United States in 1942. The United States also imports a considerable amount of wax, 1,000,000 pounds or more. In Germany, the honeycombs are made largely of ceresin. Therefore, Germany has always been forced to import much of its wax, *e.g.*, from East Africa. Russia is a very large user of beeswax and imports considerable amounts from Asia. Much of the Indian wax is exported to Great Britain and to Germany from Bengal, Bombay, Madras, Burma, and Sind. The Indian, Chinese, and Japanese insect waxes are satisfactory for technical use, but are barred from medical use by the Pure Food and Drug Act.

The uses of beeswax in the arts are numerous. Many hundreds of tons of beeswax have been used in the past in making candles in Russia, and the use of beeswax for the same purpose is a thriving though dwindling industry there today. The Roman Catholic Church uses large quantities of beeswax in the form of candles. The Church prefers the beeswax candle because of its perfumed odor when burning, whereas candles of paraffin and stearin give an offensive, greasy odor, and darken mural and other decorations.

Beeswax is used by electrotypers for taking wax impressions, and also by natural wood finishers, as it produces a well polished surface with a minimum effort of application. Root[117] records that a very satisfactory floor finish can be made by melting a pound of beeswax, and while it is cooling, stirring into it some turpentine, the amount depending upon whether a thick or thin paste is desired.

Beeswax is used in modeling flowers, fruits, illustrations of botanical specimens, and the finest work in the arts. In using beeswax for these purposes, a small quantity of lard oil or olive oil is added to make the wax more pliable. Lewkowitsch[82] states that modelling wax in Germany usually consists of beeswax 5, oil of turpentine 1 to 1½, and sesame oil ¼ to ½ parts. Beeswax is used extensively in the medical arts. Shoe pastes made in part with beeswax will withstand more dampness than those made with cheaper substitutes. The resistance of beeswax to extremes of heat and moisture make it of considerable value to the electrical industry for soaking windings of wire.

Pattern makers also use beeswax, as do manufacturers of carbon papers. Dentists use it to take impressions in the mouth. Manufacturers of precision glassware employ beeswax in the art of etching flasks, pipettes, graduates, burettes, thermometers, etc. because of the facility with which it can be cut by a stylus, and because it resists the subsequent treatment with hydrofluoric acid, and can easily be removed from the glass after etching.

Although beeswax is not used exclusively for most of the purposes mentioned, it is generally speaking the wax preferred by the artisan for these purposes. The National Farm Chemurgic Council has reported that beeswax is being used in connection with the manufacture of at least four hundred articles—from ammunition, cosmetics, and medicines, to protective coatings on airplanes.

Scale Insect Waxes

Family Coccidae

There are a number of genera of the family of *Coccidae* that furnish waxes, although only two have been of economic importance thus far, namely *Coccus ceriferus*, the source of the Chinese insect wax of commerce, and *Tachardia lacca*, furnishing stick-lac wax, or in its refined form commercial shellac wax.

In the order *Coccidae* there is a sub-family *Coccinae*, in which the "scale" is merely the thickened surface of the insect, instead of being a separate housing of the body. The *Pulvinaria* is a genus which secretes a mass of cottony material in which the insect places its eggs. The genus *Coccus* belongs to the *Coccinae*, as do also *Brahmea*, *Tachardia*, *Cerococcus*, and *Pulvinaria*. These insects are referred to as "coccins."

The scale insects which have a wax shell housing separated from the body are known as "coccids." *Ceroplastes* is the best known genus; others furnishing waxes are *Iceria*, *Sasakiaspis*, *Prontapsis*, and *Tachardina*. The character of the wax will change somewhat depending upon the species of host plant on which the insect feeds, these plants in the far East being privet, citrus fruit, tea, etc. Most of the studies of the waxes have been made in India, China, and Japan. The eggs deposited by the scale-insect may be transferred from one host to another to secure the best commercial yields, as in the case of the *Coccus ceriferus.*

Chinese Insect Wax

Chinese insect wax, also called Chinese wax and China wax, or "pe-la" by the Chinese, resembles spermaceti in whiteness and crystalline appearance, but it is of greater hardness and friability. The wax is the product of the scale-insect, *Coccus ceriferus,* Fabr. (*Coccus pela,* Westwood). The insects are deposited on the twigs and branches of the Chinese ash, *Fraxinus Chinensis,* Roxburgh. The insects closely infest the twigs and become imbedded in a waxy material, which when scraped off with the insects, constitutes the crude wax. It is purified by melting and straining. Cooper[139] in his "Travels of a Pioneer" in China tells of its production in the manner described below.

The seat of the industry is in the province of Szechwan (Sze-chuen) in China. The "wax trees" are cut down to a height of eight feet leaving no branches, the trunks sending forth shoots in the spring. The insects are cultivated in a different province, that of Yunnan. Here the brown pea-shaped scales containing the larvae of the wax insect are developed on an evergreen *Ligustrum luditum,* Ait (large-leaved privet) as a host. From Yunnan vast quantities of eggs or scales are shipped to Szechwan each year, where they are received in little balls the size of peas. These are suspended, enclosed in young leaves, on the shoots of the tree in March. In about two months the larvae emerging from the packets feed on the leaves. They soon attain the size of small butterfles, spreading themselves in immense numbers over the branches, which are so whitened by them as to seem covered with feathery snow. The grub, as it advances to the chrysalis form, buries itself in a white secretion which covers all the branches an inch thick. These are then cut off near the stem and divided into small pieces, which are tied in bundles and put in large cauldrons, where they are boiled in water till the wax melts and rises to the surface. The wax is then skimmed off and run into moulds, where it hardens. It is said that 1500 insects produce 1 to 2 grams of wax. A pound of larvae scale will produce 4 or 5 pounds of wax.

Although Chinese insect wax has been defined as a product of *Coccus ceriferus,* there is another variety produced by *Brahmea japonica,* according to Huminski.[65] He states that the wax from *Coccus ceriferus* is a yellow wax of which *ceryl alcohol* ($C_{27}H_{55}OH$) and *cerotic acid* ($C_{27}H_{54}O_2$) are the principal constituents; these occur in the form of the ester, *ceryl cerotate.* The *Brahmea japonica* wax is a white wax which contains, in addition to the ceryl alcohol and cerotic acid components, a non-saponifiable, stable, crystalline hydrocarbon, ***heptacosane*** $C_{27}H_{56}$.

Chinese insect wax is usually defined as yellowish-white, very hard, brittle, fibrous, crystalline, and translucent. The wax has a specific gravity of 0.950 to 0.970 at 15°, and 0.809–0.811 at 98–99.°[129] It has no characteristic smell or taste. Chinese wax melts at 80.5–83.0° (177–181° F). The wax is only slightly soluble in alcohol and ether, but is freely soluble in hot petroleum spirits and in benzene; it is insoluble in water and in cold turpentine. Chinese wax has an acid value of only 0.2–1.5, a saponification value of 78–93, and an iodine value of about 1.4.

The identification of the alcohol and acid components in Chinese insect wax has been a subject of considerable discussion, however. According to Gascard,[47] Brodie has shown that Chinese wax is almost exclusively formed of the ester of ceryl alcohol and cerotic acid, to which he assigned the formulas $C_{27}H_{56}O$ and $C_{27}H_{54}O_2$ respectively. Marie of Paris, Gauthier-Villars, in a thesis published in 1895, assigned the formula $C_{25}H_{50}O_2$ to the cerotic acid found in beeswax, and gave the acid a melting point of 77.5°. Gascard[47] in 1920 declared that the cerotic acid in Chinese wax was not of the same composition, but that Brodie had identified the same acid in beeswax and has assigned it the formula $C_{27}H_{54}O_2$ (m. 78°). Gascard prepared cerotic acid by the acetic bichromate oxidation of ceryl alcohol isolated from Chinese insect wax, and found the acid to have a melting point of 81.5–82° as crystallized from benzene. The highly purified wax or ester, *ceryl cerotate,* melts at 84°, and may be converted to calcium cerotate, and then changed to cerotic acid by treating it with glacial acetic acid. The cerotic acid had a melting point of 82–82.5°, and crystallized from benzene in little white plates. Gascard, like Brodie, concluded that Chinese insect wax consists mainly of the ester of ceryl alcohol $C_{27}H_{56}O$ (m. 79.5–80°) (49%) combined with cerotic acid, $C_{27}H_{54}O_2$ (m. 82–82.5°) (51%). The acid found in beeswax and designated by the same name Gascard believed to be different, since it melts at 77.5° and appears to have the formula $C_{26}H_{52}O_2$ or $C_{25}H_{50}O_2$.

Huminski[65] in 1935 referred to the older formula $C_{26}H_{54}O$ for *ceryl alcohol* as noted by Henriques,[58] and then assigned the formula $C_{27}H_{56}O$ as the correct one. However, it is to be noted that in 1920 Gascard[47] had already confirmed Brodie's assignment of $C_{27}H_{56}O$ to ceryl alcohol, by isolating it in pure crystalline plate form (m. 79–80°). In 1935 Collins[30] separated the *n*-aliphatic acids present in Chinese insect wax by fractional distillation of the ethyl esters in 0.5 mm vacuum. Mixtures of C_{26}, C_{28}, C_{24}, and C_{30} acids were obtained. Of these esters 22 per cent of the higher fractions melted between 62.5° and 70° (indicating *neomontanic* and *myricinic acids*). The presence of the C_{30} acid had not been reported previously.

If the composition of Chinese insect wax were almost entirely *ceryl cerotate* (*b*), $C_{26}H_{53}CO \cdot OC_{27}H_{55}$, as often reported, the ester value would approach 71.1. The actual ester value of the wax is appreciably higher than this, generally above 78 and sometimes as high as 92. Although the wax contains a little resin this would hardly account for the high ester value. Collins' separation of a C_{24} acid does account for a lower molecular weight ester than the C_{27} ceryl cerotate. The lower ester is undoubtedly ceryl lignocerate, which has an ester value of 76.5.

The chemical composition of Chinese insect wax appears to be about as follows:

Esters of Monobasic Acids: 95–97 per cent
  myricyl lignocerate (2%), m. 83°
  neomontanyl lignocerate, m. 81°
  ceryl lignocerate, m. 79°
  ceryl cerotate (*b*) (20%), m. 84°
  ceryl neomontanate (20%), m. 85°

Resins: less than 1 per cent

Free Wax Acids: ½–1 per cent
  cerotic acid (*c*), (C_{26}, C_{28}), m. 82–82.5° (G)

Free Aliphatic Alcohols: less than 1 per cent
  myricyl alcohol, m. 80.0° (G)

Hydrocarbons: less than 1 per cent
  heptacosane, m. 59.5°

Uses of Chinese Insect Wax. Chinese insect wax is marketed in thick round cakes weighing 16 to 20 kilograms. It is of considerable value in China and Japan, where it is used in the manufacture of candles and medicaments. Stock[129] says that it is used as a coating material for Chinese yellow candles. It is also used in treating silk and cotton fabrics; in the sizing and glazing of papers; and for electrical insulation. It is seldom used in the shoe cream and polish industry, but is used to a limited extent in the manufacture of furniture polishes when it is freely obtainable as an article of commerce. The wax foundation of one American polish is said to have consisted of carnauba wax 1, African beeswax 1, and Chinese insect wax 1 part.

Shellac Wax

This wax is derived from the Lac insect, *Carteria lacca*, mixed with non-waxy substances, such as resins, coloring and other matters. An analysis of the actual constituents of crude lac shows the following amounts of wax: Stick-lac 6.0 per cent, seed-lac 4.5 per cent, shell-lac 4.0 per cent. The lacs are only partially soluble in alcohol, because the wax constituent will not dissolve in alcohol or methylated spirit at ordinary temperatures. Therefore, the wax can be made a by-product in the preparation of spirit lac. Stick-lac is the name given to the crude lac just as it is removed from the trees. The crude lac is melted in water and beaten to deprive it of its red color, and the resulting seed-lac goes through a process of refinement

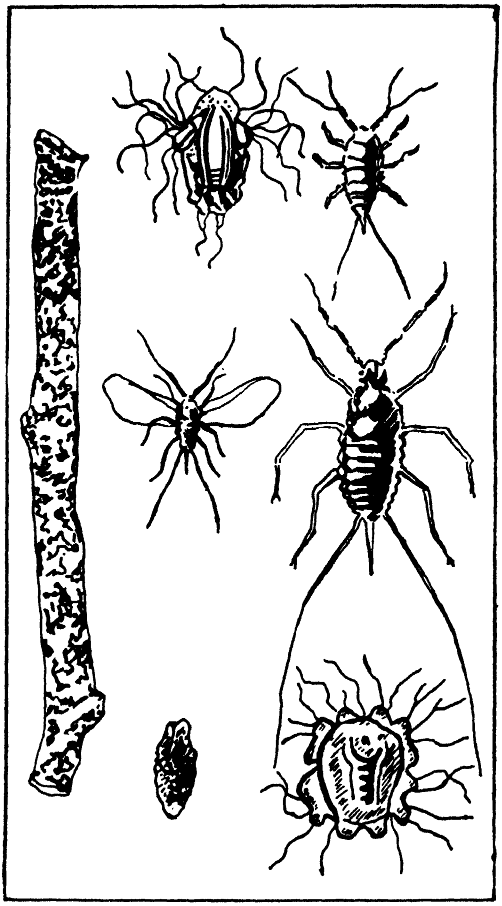


FIGURE 3. Lac bugs attached to the branch of a Lac tree. Male, female and young insects greatly magnified.

to produce shell-lac or orange shellac. In making refined (dewaxed), bone dry, bleached shellac about 3 or 4 per cent of wax is obtained, based on the quantity of raw lac used.

To dewax shellac spirit varnishes, the London Shellac Research Bureau recommends the following procedure. Wax containing shellac varnish (75 gal) is mixed with 25 gal of white spirit (d_{20° 0.7924); the mixture is heated to 70 – 80° for a half hour; then the heating is discontinued and the mixture is allowed to cool and settle. The wax particles swell and rise to the surface of the varnish with the white spirit, and the clear varnish can be run from the bottom of the vessel after 24 hours (85 to 90 per cent yield of clear varnish). The white spirit can be used at least three times for dewaxing fresh batches of varnish. If the mixture is not heated, at least 48 hours will be required for the wax to separate. For rapid separation, the concentration of lac in the varnish is critical, 3 lbs of lac per gallon of industrial methylated spirit being the optimum. For example 28, 36, 40 and 48 hours are required for the wax to rise to the surface when varnishes 2.5, 4.5 and 6 lb "cut" per gallon, respectively, are treated with white spirit with the heating procedure.

If shellac (containing wax) is shaken with two organic solvents, one of which dissolves the shellac, *e.g.*, alcohol, and the other, of lower specific gravity, which dissolves the wax, *e.g.*, benzine, separation of the wax may be effected. Agitation with these solvents is done in the cold and is continued until all the shellac has dissolved. Upon standing, the mixture is separated into three layers. At the top is found the wax in benzine, at the bottom shellac in alcohol, and there is an intermediate layer of undissolved suspended wax particles. This is the method proposed by Marwedel.[98]

Shellac wax has excellent gloss-producing qualities somewhat similar to those of carnauba. The specific gravity of ordinary shellac wax is 0.971–0.980 at 15.5°; the melting point 74–78°, or lower than that of carnauba wax. The acid value is 12.5 to 16.0, saponification value 100–126, ester value 84–114, unsaponifiable matter 72 to 76 per cent, and ash 0.08 per cent.

Shellac wax is practically insoluble in alcohol at room temperature, only 0.067 gram dissolving in 100 ml of 95 per cent strength. It is partially soluble in diethylene chloride, 1.19 grams dissolving in 100 ml of solvent at 37°.

The following analysis is one furnished by Gillespie-Rogers-Pyatt Co., New York, of a sample of shellac wax of good quality: sp. gr. at 20° 0.972, m.p. 82° (closed capillary), 80° (falling drop), saponification value (in butanol solution) 46.7, direct acid value 1.2, iodine number (Wijs) 1.25, ash 0.045 per cent, hot kerosene-insoluble 0.072 per cent, hot choloroform-insoluble 0.034 per cent, moisture and volatile 0.21 per cent, ester value 45.5.

Shellac wax has a dielectric strength varying from 356 to 418 volts per mil, which is much lower than that of the shellac. However, it has a breakdown voltage which compares favorably with that of shellac, and the presence of the wax in the shellac facilitates proper molding in the electrical industry.

Gascard[48] in examining the residual wax of stick-lac (*Tachardia lacca*), after the resin was extracted with alcohol, found it to yield an ester, *lacceryl laccerate* (m. 94°) which on saponification gave *laccerol* (lacceryl alcohol) ($C_{32}H_{65}OH$) in rhomboidal plates (m. 88°) and *lacceric acid* ($C_{31}H_{63}COOH$) in rhomboids (m. 95°–96°), and also proved the chemical structure of lacceryl laccerate.

A shellac wax from Madagascar is exported under the name of "Lokombitsika," and has been reported to be that formed by the insect *Gascardia madagascariensis.* The resin produced from this insect is used for making varnish, but the wax as marketed is said to have only 12 per cent of the true wax ingredient.

Uses of Shellac Wax. True shellac wax commands a high price, and is employed in the electrical industry. The demand for refined shellac wax exceeds the supply, which in the United States does not exceed 50,000 lbs a year. The high melting point and electrical insulation value favor its use in electrical appliances. In shoe creams the addition of a little shellac wax to an otherwise ordinary formula containing montan wax and paraffin is a means of producing a high luster. Shellac wax for such purposes is said to be frequently adulterated with Chinese insect wax, tallow, resin and montan wax.

The composition of stick-lac wax when substantially free from shellac resin is about as follows:

Esters of Wax Acids: 60–62 per cent
- ceryl lignocerate, m. 79°
- ceryl cerotate, m. 84°
- lacceryl laccerate, (10–12%)
- ceryl aleuritate,* (less than 1%)

Free Wax Acids: 1 per cent
- lacceric acid, m. 95–96°

Free Wax Alcohols: 35–35 per cent
- neoceryl (tachardiacerol) m. 80.1° (Tschirch)
- lacceryl, m. 88°

Hydrocarbons: 2–6 per cent
- pentacosane (tachardiacerin) (2%)
- hentriacontane

*Aleuritic acid is • 9,10,16-trihydroxypalmitic acid, $HO \cdot CH_2 \cdot (CH_2)_5 \cdot CH(OH)$, $CH(OH) \cdot (CH_2)_7 \cdot COOH$

Aleuritic acid exists in the combined state as an ester, with a melting point of 82°. This would more or less correspond to the ceryl ester. The commercial shellac waxes have a higher ester value than the wax above cited because of the presence of the aleuritic resins.

Miscellaneous Coccin and Coccid Waxes

Wax of Coccin, Erytherus Pela. Teng-Han Tang *et al.*[133] of China reported the results on the identification of an insect wax other than the well known Chinese insect wax, from which it greatly differs. The insect is of the family *Coccidae,* growing in the neighborhood of Tsingtao. Either the same or a similar wax had been reported by Koyama[76] as having been derived from the wax-producing insect *Erytherus pela,* Chevannel, grown on the host plant *Ligustrum ovalifolium,* a species of privet. The wax was extracted with ether and benzene with a yield of 87 per cent. Teng-Han

Tang gives the following constants for the coccid wax: density 15° 0.9683 m.p. 50–51°; refractive index at 60° 1.4804; acid value 35–36; saponification value 146–150; iodine number (Hanus) 35 to 36; Reichert-Meissl number 6.5; Polenske number 4.3; unsaponifiable substance 26.9 per cent. The wax consists principally of wax esters, *ceryl cerotate* with less *melissyl cerotate.* Much of the *cerotic acid* is in the free state. An unsaturated acid is also indicated. Hydrocarbons are present to the extent of 21.8 per cent. *Cholestene* ($C_{27}H_{46}$) is present to the extent of 4.7 per cent. The total alcohols (combined) amount to 7.45 per cent calculated as *ceryl alcohol.* The total *cerotic acid* (m. 78°) free and combined amounts to 35.7 per cent, and the unsaturated acid (resin acid) 29.9 per cent. The principal hydrocarbon is *hentriacontane.*

Koyama[76] refers to a similar wax collected in the province of Echigo in Japan, and states that the wax acids contain 70 per cent of isocerotic acid, 15 per cent of cerotic ($C_{26}H_{52}O_2$) a C_{28} acid, and 15 per cent of the lower fatty acids. No behenic acid was found. The principal unsaponifiable substances are *isoceryl alcohol* (C_{27}) and a smaller amount of *melissyl alcohol.* The latter exists as *mellisyl cerotate* ($C_{30}H_{61} \cdot CO \cdot OC_{27}H_{55}$). The isocerotic ($C_{27}H_{54}O_2$) melts at 82°. Lower alcohols were found to the extent of 10 per cent, and they were identified as *hexadecyl, octadecyl,* and a lesser amount of *tetradecyl alcohol.*

Wax of Coccus Cacti. Although *Coccus cacti* is best known as the cochineal insect that produces a dye of value as a pigment and as a medicine, it is of interest to note that the coating of its shell contains a wax which gives it a silvery appearance. As early as 1885 Liebermann[85] isolated this wax, gave it the name of coccerin, and assigned to it the formula $[C_{30}H_{60}(C_{31}H_{61}O_3)_2]$. Silver cochineal wax contains a fat (stearin, olein, and fatty acids); a hydroxy acid known as *cocceric acid* ($C_{31}H_{62}O_3$, m. 92–93°) *coccerin* 0.5–1.7 per cent; and *myristin.* Coccerin is now considered as an ester of one mole of cocceric acid with one mole of the dihydric alcohol, *cocceryl alcohol* $[C_{31}H_{60}(OH)_2]$.

The red cochineal insect, *Pseudococcus cacti,* a native of Mexico, feeds on the cactus plant, *Nopalea cochenillifer,* L., commonly called "copal." During the rainy season, a number of the females are preserved under cover, upon the branches of the plant, and after the rains have stopped they are distributed upon the plants without. They perish quickly after having deposited their eggs. These, hatched by the heat of the sun, give origin to innumerable minute insects, which spread theselves over the plant. The females, which moved about before fecundation, bury themselves in the leaves, increase rapidly in size, and finally appear more like excrescences on the plant than animated insects. They are now gathered for use by detaching them with a blunt knife, a quill, or a feather. They are destroyed either by dipping them, enclosed in a bag, into boiling water or by the heat of a stove. If destroyed in the former manner they are subsequently dried in the sun. Cochineal is the source of carminic acid, which has a brilliant purple-red color.

The wax of the shell is of interest because of its peculiar chemical make-up. It contains an unusual ketonic alcohol, namely, 15-keto-*n*-tetratriacontanol [$CH_3 \cdot (CH_2)_{18}, CO \cdot (CH_2)_{13} \cdot CH_2OH$]. It also contains the corresponding ketonic acid and ester, together with triacontanic acid. Chibnall[26] considered 15-ketotetratriacontanol to be *cocceryl alcohol,* and *coccerinic acid* as a mixture of *13-ketotriacontanic acid* and *triacontanic acid.*

A coccin insect named *Coccus axin* furnishes a wax known as *axin wax.*

Ceroplastes Waxes. Perhaps the first coccid wax of the ceroplastes genera to attract attention was that of the scale-insect, *Ceroplastes rubens,* Maskell.[73] The insect was found to inhabit two species of acacia which are widely distributed on the banks of the Senegal river, in French Equatorial Africa. The white insect wax of India is believed to be derived from the same species of insect which infests the twigs of a shrub or tree, *Terminalia arjuna,* and is not at all abundant. The wax is known as *Arjun wax,* the name being taken from its host. The wax occurs on the twigs in small mounds of a buff color, in which form it is collected. The female of the coccid insect is always without wings and has either a scale-like or a gall-like form; it is covered with scales of wax, which may be in the form of a powder, of large tufts or plates, of a continuous layer, or of a thin scale. Beneath this protecting substance lives the insect. All scale-insects are plant-feeders, and obtain liquid food by means of suction. They are injurious to the plants on which they feed, but this is compensated by the economic value of the insect products obtained. A closely allied species is *Ceroplastes ceriferus,* And.

Arjun wax is moderately hard and brittle and of a rather pleasing odor. It melts at 55 to 58°, or at a much lower temperature than China wax. The density is 1.03 at 15°, and 0.997 at 40/40°. According to Kono,[73] *C. ceriferus* has a density of 0.997 at 15°, and a melting point of 58–58.5°. Koyama[76] reported the chemical constants of the *C. rubens* cultivated on tea trees as follows: saponification value 152.8, acid value 22.9, iodine number 76.3. Kono,[73] however, reports somewhat different constants for the wax of *C. rubens.* Koyama found that the wax isolated from coccid scale grown on citrus trees was of a larger yield, 70 per cent, and had the following constants: d40/40° 0.9921 m.p. 55–57°, saponification value 126, acid value 46.6, iodine number 130.5. The citrus coccid scale wax, according to Koyama[76] who isolated its constituents, is composed of *melissic, ceromelissic* ($C_{33}H_{66}O_2$, m. 94°), *ceroplastic* ($C_{35}H_{70}O_2$, m. 96–98°), and a resin acid ($C_{22}H_{34}O_2$). The alcohols are *melissyl, ceromelissyl,* and *ceroplastyl alcohol,* all primary alcohols. No *ceryl* or *isoceryl alcohol* or coresponding acids were found. On the other hand Kono reports the presence of ceryl alcohol.

The studies of Kono[73] are tabulated below so that a ready comparison may be made of the different coccid waxes of the genus *Ceroplastes.* The method followed by Kono in isolating the ingredients was to separate the wax into alcohol-soluble and -insoluble parts. The cold insoluble part, which was resin-free, was recrystallized from hot alcohol, from which in the case of *C. rubens,* Mask., *melissic acid, ceryl alcohol,* and an unknown *cyclic alcohol* ($C_{17}H_{15}O$, m. 68°) were isolated. From the alcohol-soluble part a red colloidal mass was obtained, from which a resin acid resembling *abietic acid* and a *resinol* were isolated. The resin acid had a melting point of 163°. The chemistry of the resin acids and resinol has been recently clarified by Kono, and these identified components of the ceroplastes waxes are set forth in the tabulation.

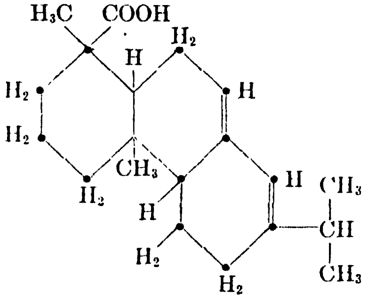
Ceryl melissate is without doubt a mere mixture of the monomers, *ceryl myricinate* (C_{26},C_{30}) and *octacosyl laccerate* (C_{28},C_{32}), the alcohols and acids giving the C_{27} and C_{31} dimers when freed in the analysis.

The differences in the Ceroplastes waxes, based on the studies of Kono,[73] are given below:

	C. rubens, Mask.	*C. ceriferus,* And.	*C. floridensis,* Comst.
Density at 15°	1.030	0.9975	1.012
Melting point	55–58°	58–58.5°	49–50°
Acid value	63.4	47.2	40.9
Saponification value	139.0	139.4	97.5
Ester value	75.5	92.2	56.6
Acetyl value	23.8	57.6	80.2
Iodine number	90.3	85.3	61.6
Neutral fat	36.5	19.4	27.7
Unsaponifiable	20.0	26.9	22.4
Melissic acid	detected	detected	detected
Psyllostearillic acid	——	detected	detected
Cerotic acid	——	——	——
Ceryl alcohol	detected	detected	detected
Isoceryl alcohol	——	——	——
Cyclic alcohols	$C_{11}H_{18}O$ (b_4 120°)	$C_8H_{14}O$ (b_{10} 95°)	$C_8H_{14}O$ $C_{12}H_{22}O$ (b_3 140°)
Melissate of cyclic alcohol	m. 68°	detected	——
Ceryl melissate	m. 86°	m. 85–86°	——
Resinol	$C_{20}H_{32}O$ (rubenol, b_2 190°)	$C_{16}H_{26}O$	——
Resin acids:			
I.	$C_{20}H_{32}O_2$ (rubeabietic) (m. 163°)	$l-C_{12}H_{22}O_2$ (b_3 72–74°) $[\alpha]\frac{20°}{D} - 34.77$	$d,l-C_{30}H_{52}O_4$ inactive
II.	$C_{20}H_{30}O_2$ (rubenic) (m. 88°)	$d,l-C_{38}H_{60}O_7$ (m. 57°)	$d-C_{33}H_{52}O_5$ $[\alpha]\frac{12°}{D} + 81.56$

	C. rubens, Mask.	*C. ceriferus*, And.	*C. floridensis*, Comst.
III.	——	*d,l* – $C_{28}H_{40}O_2$ (m. 43–44°)	*d* – $C_{20}H_{30}O_3$ (m. 177°) $[\alpha]\frac{13°}{D} + 16.35$
IV.	——	*d* – $C_{57}H_{87}O_{10}$ (m. 33-38°) $[\alpha]\frac{30°}{D} + 74.62$	*d* – $C_{12}H_{22}O$ (b_3 140°) $[\alpha]\frac{10°}{D} + 46.44$

NOTE: The optical rotation of rubeabietic acid is dextro, whereas abietic acid (m. 171–3°) derived from colophony is levo. $[\alpha]_D - 86.9$. Abietic acid is a carboxylic acid of 1-methyl-7 isopropyl perhydrophenanthrene ($C_{20}H_{30}O_2$) of the following structural formula:



The approximate composition of the wax of *Ceroplastes rubens*, Arjun wax, appears to be about as follows:

Neutral Fats: 36–37 per cent
palmitin, stearin, olein, etc.

Alkyl Esters: 20 per cent
ceroplastyl cerotate, m. 90° (?)
lacceryl cerotate, m. 89° (?)
myricyl laccerate, m. 91°
ceryl melissate (C_{27}, C_{31}), m. 86°

Free Wax Acids: 3-4 per cent
ceroplastic acid (C_{34}, C_{36}), m. 96–98°
ceromelissic acid (C_{32}, C_{34}), m. 94°
melissic acid (C_{30}, C_{32}), m. 90°

Resins: 34 per cent.
rubenol (resinol), b_2 190°
rubeabietic (resin acid), m. 163°
rubenic (resin acid), m. 88°

Lactones: 1–2 per cent
4-methyl-4-decanolactone ($b_{4.5}$ 120–125°) ($C_{11}H_{18}O$)

Hydrocarbons: 3-4 per cent
hentriacontane
cyclic (cholestene)

Esters of Cyclic Alcohols: (m. 68°)
myricyl and lacceryl esters of cyclic alcohol, $C_{17}H_{18}O$

Wax of Coccid *Ceroplastes Grandis*. Mollan,[105] of Brazil, reports on a coccid, *Ceroplastes grandis*, which feeds on the tree *Mimosa acutifolia*,; when collected in dry weather the insect contains 8 per cent of a white wax soluble in petroleum ether, or 10 per cent of a yellow wax soluble in ether. The density of the wax is 1.0002 at 25°, and it melts at 49°. It has a saponification value of 91.0 and an acid value of 30.3. It contains 65 per cent of unsaponifiable matter.

Wax of *Pulvinaria Horii*. In 1933 Kono[72] reported on the coccin wax of *Pulvinaria horii*, Kuw. The following constants are noted: d_{15} 0.901; m.p. 72.5–73°; acid value 12.3; saponification value 117.1; ester value 104.7; and iodine number 6.5. The wax consists primarily of ceryl cerotate (m. 75–76°), a small amount of cerotene ($C_{26}H_{52}$, m. 56.5°), an unknown *cyclic alcohol* ($C_{22}H_{36}O$), and an unknown *resin acid*, ($C_{14}H_{28}O_2$,$b_{2.5}$ 72–74°).

Wax of Coccid, *Iceria Purchasi*, Mask. Kono and Maruyama[72a] in 1933 reported on the composition of the wax from the shell of the scale-insect, *Iceria purchasi*, Mask. This insect generally feeds on the citrus trees as its host. A number of years ago this same species of insect threatened ruin to the orange plantations in California, where it had accidentally deposited. The blight had to be checked by parasitic insects, chiefly larvae of a lady-bird beetle imported from Australia.

The waxy substance from the insect was extracted with benzene, and the following constants obtained: density$_{15}$ 0.914: m.p. 78°; acid value 61.2; saponification value 157.5; ester value 96.3; iodine number (Hanus) 56.2; acetyl value 118.3; neutral fats 67.25 per cent; and unsaponifiable matter 31.5 per cent. The waxy substance after refining was determined to be of the following percentage composition: *o-hydroxy-benzaldehyde* 0.2; *ceryl alcohol* 9.9; *isoceryl alcohol* 1.7; *carnaubyl alcohol* 0.7; *cerotene* 0.3; *octadecyl, tetradecyl* and *cetyl alcohol*; 0.6; *cerotic acid* 35.5; *palmitic acid* 27.3; *resin acid* $C_{10}H_{16}O_4$14.6; *melissic acid* 0.13; and *stearic acid* 0.8.

Wax of Coccid *Sasakiaspis Pentagona*. The insect body of the scale-insect, *Sasakiaspis pentagona*, Tar., is reported to contain 26.8–27.0 per cent of wax, the composition varying to some extent with the kind of host plant. The percentage composition of the wax is of the following order: *melissyl alcohol* 27.5; *melissic acid* 13.0, *cerotic acid* 38.8, and *resinol*, $C_{10}H_{18}O$ 4.2.

Wax of *Cerococcus Muratae*. In 1933 Kono reported on the wax of the insect *Cerococcus muratae*, Kuw. The wax is a dark reddish-brown resin. It melts at 77–78° (much higher than the melting points of the Ceroplastes waxes), has d_{15} 0.906, acid value 25.2, saponification value 212.8, ester value 187.6, iodine value 15.6, acetyl value 110.4, neutral fat 72.96 per cent, unsaponifiable matter 15.79 per cent. The constituents in a hot alcoholic extraction of the wax were isolated and found to be *cerotic acid*

(m. 78°) and *ceryl alcohol* (m. 78°). *Cerotic acid, isoceryl alcohol,* and an unknown hydrocarbon (m. 47.5°) were obtained from the portion insoluble in hot alcohol. An *unidentified acid* ($C_{19}H_{36}O_4$, b_3 145°, m. 12–12.5°) was isolated from the portion soluble in cold alcohol.

Wax of *Prontaspis Yanonensis*. Kono[72b] in 1936 reported on a coccid wax obtained from the insect *Prontaspis yanonensis,* Kuw, the body of which consists of water, reducing sugars, cellulose, lignin, minerals, wax, pentosans, proteins, with traces of galactan and mannan. The wax content was found by Kono to be 36.84 per cent. The wax has the following constants: d_{15} 0.939, m.p. 79–81°, acid value 14.6, saponification value 86.5, ester value 72.0, iodine value 13.1, acetyl value 9.8, neutral fat 74.80 per cent, unsaponifiable matter 26.20 per cent. Constituents are *ceryl alcohol* 3.5, *cerotic acid* 25.0, *lauric acid* 2.0, *melissyl alcohol* 34.5, a resinol ($C_{10}H_{18}O$) 8.5, and a distillate by steam distillation 0.5 per cent.[72b]

Wax of *Tachardina Theae*. In 1939 Kono and Maruyama[74] reported on the coccid wax of *Tachardina theae,* Green et Mann, found only in Formosa. From 140 parts of its wax they isolated *melissyl alcohol* 5.7, *ceryl alcohol* 6.6, *cocceric acid* 0.7, *melissic acid* 15.4, *myristic acid* 33.6, *n-hentriacontane* 0.7, *dodecenoic acid* 8.4, and *tetradecenoic acid* 24.4. The dihydroxy acids of the latter, *dihydroxy-decenic* and *dihydroxy-tetradecenoic* melts at 115.2° and 127.5°, respectively. Glycerol and resin were also found.

Wax Constituents of Plant Lice

A number of ordinary parasitic insects excrete wax in minute amounts. These include psylla and aphids. Psylla are particularly worthy of mention, since the waxes contain C_{32} alcohol, acid and ester. *Psyllyl alcohol* ($C_{32}H_{64}O$) was first discovered in *Psylla alni,* and *Psylla buxi,* R. also appears to contain the ester of *psyllic acid* and psyllic alcohol, together with C_{30} and C_{28} compounds in lesser amounts. The wax melts at 89.6 to 90.1°, and on hydrolysis gives an acid (m. 92.7°) (ethyl ester m. 68.8°) and an alcohol (m. 86.2°) (acetate m. 68.7°).

Cocoon Silk Wax

There is a waxy substance in the cocoon silk fibers of the *Bombyx mori.* According to Masami[99], this wax is extractable with ether from the cocoons, and when the extract is dried it is orange in color and easily pulverized. Eighty per cent of it is soluble in boiling alcohol. The crude wax melts at 65°. After purification by crystallizing several times from boiling alcohol the product consists of 63 per cent of unsaponifiable substances and 37 per cent of fat and wax acids (m. 68–69°). The refined wax has an acid value of 13.4, saponification value 110.8, and iodine number 4.5. The unsaponifiable of the refined wax contains 81.9 per cent of higher alcohols, 18.1 per cent of hydrocarbons, and no sterol. The unsaponifiable melts at 84°, and partly dissolves in acetic anhydride. The soluble part contains ceryl and myricyl alcohols, and the insoluble part contains the hydrocarbons. The unsaponifiable portion purified from amyl alcohol and fuming sulfuric acid is mainly *hentriacontane.* The fat and wax acid portion has a molecular weight of 186.7 and a neutralization value of 300.5. The part which is insoluble in water is mainly *melissic acid* accompanied by some *stearic* and *palmitic acids.* The fatty acids soluble in water have a molecular weight of 140.4 (caprylic acid, 144.2).

Part II: Waxes from Animals

Classification of Animal Waxes

Animal waxes may be classified as (1) those obtained from land animals, and (2) those obtained from marine animals. The most important wax of the land animal group is *wool wax,* commonly called wool fat, or in its highly refined form, *lanolin,* of the second group, the most important wax is *spermaceti.* Both these waxes are extensively used in the arts and industries. Marine animal waxes may be divided into two types: (a) solid marine waxes and (b) liquid marine waxes. In the liquid type we have *sperm oil* and closely allied oils, all of which are free from glycerides, or nearly so. The liquid waxes usually contain considerable amounts of esters of unsaturated alcohols and acids, whereas the solid waxes contain only esters of saturated components.

SOLID LAND-ANIMAL WAXES

Wool Fat (Wool Wax)

Wool wax, or *wool fat,* is the purified fat of the wool of the sheep. Lewkowitsch classified wool fat as a wax on the basis of its chemical composition, although commercially it is seldom so referred to.

Origin of Wool Fat. As it comes from the sheep's back, wool is called by the scourer "wool in the grease." This wool is then turned out clean with a moisture content of 16 per cent of the weight of the clean, dried wool. If washing is done preliminary to sheep-shearing, the washed wool, freed from yolk, will consist of about 73 per cent clean wool, 13 per cent water, 5 per cent soil, 4 per cent fat, 2 per cent potassium salts, and 2 per cent of foreign organic matter. Unwashed wools contain 45 to 62 per cent of clean wool, 9 to 13 per cent water, 9 to 16 per cent soil, 10 to 24 per cent fat, 4 to 6 per cent potassium salts, and 4 to 8 per cent of foreign organic matter. In wool grease the "suint" is the saponified portion which contains the potassium salts. It is the wool fat which is recovered to be placed on the market as *lanolin.*

Wool fat and suint are estimated on the basis of percentages on the weights of the clean dry wool.[39]

Wool	Wool fat (%)	Suint (%)
Australian	35 to 46	14 to 23
African	28 to 41	12 to 26
Peruvian	9 to 14	29 to 35
English	9	27

The neutral portion derived from wool grease is largely composed of cholesterin esters of several fatty acids and higher alcohols.

Lanolin. The United States Pharmacopœia[140] defines lanolin as the purified fat of wool of the sheep, *Ovis aries*, Linne, mixed with not more than 30 per cent of water, whereas it defines wool fat as the purified fat of the wool of sheep (*Ovis aries*, L.), freed from water. The latter is commonly referred to as *anhydrous lanolin.* The British Pharmacopœia[19] defines *wool fat* as "the purified cholesterin—fat of sheep's wool," a definition which may be more expressive than that of the U.S.P.

Recovery of Lanolin from Scoured Wool. Scouring the raw wool is done with the aid of warm soda or lye and a considerable quantity of water. In England the recognized type of merino wool-washing machine is the fork-frame bowl.[39] Three to five of these machines are employed for steeping, scouring, rinsing, etc. The emulsion method of wool scouring is universal in England; but in North America the solvent method is largely in use, the solvent (benzine) being recovered by volatilizing and condensing so that it may be used over and over again.

In the emulsion method the waste liquor or lye is passed through a centrifugal machine in which the dirt and fat are separated, and the cleansed soap liquor is continuously piped off into the vat which serves for the acidulation, to be recovered as a by-product. The raw fat is then heated with water (49 to 53°) so that it can be skimmed from the surface and collected or cooled. For further purification it can be treated in the centrifugal machine in melted condition, or it can be separated by suitable solvents and the solution separated from the residue by filtration. The solvents can be recovered by distillation. After the fat has been cleaned, it is kneaded with water for a long time to obtain a perfectly white neutral, colorless ointment, *lanolin.* From the deposit in the lowest part of the centrifugal machine a further portion of lanolin may be recovered.

Wool grease varies in composition according to whether the suds from wool scouring are kept separate or are mixed with the soap suds from the scoured woolen goods in the woolen mills, where the wool is washed, spun, and woven. In the Bradford area of England something like 14,000 tons of grease a year are scoured from raw wool and recovered. About one-third of the wool grease is recovered by the wool combers themselves; and two-thirds, by arrangement with local authorities, is dumped into the sewers and recovered by the Bradford Sewage Disposal Works, as it emanates from a large number of small wool-combing firms in that area. The product of the wool combers, or *straight grease,* if of better grade, is worked up into such products as lanolin, lubricating greases, metal-coating compositions, paints, etc. The *sewage grease* amounted to 9000 tons in 1940, and its economic disposal presented a problem, as its sale in Continental Europe had been discontinued.

On distillation the sewage grease yields an oil (*wool oleine*), a wax (*wool stearine*), and pitch. The wool stearine finds a ready market, but the demand for oleine and pitch is limited. The grease itself was generally recovered by first acidifying the effluent, filtering the sludge hot and allowing the filtered grease and liquor to separate.

The yield of wool fat in commercial operations is dependent upon the efficiency of the method employed in its recovery. Modern centrifuges have stepped up the yield from 20 to 30 per cent to 60 to 70 per cent when operating at a temperature of 70 to 75°. Naturally, larger fat losses or poorer yields are obtained from unusually dirty wools. Lewkowitsch[82] states that the commercial yield of wool fat from New Zealand wool is 16.6 per cent, from Australian wool 16.0 per cent, from South American wool 13.2 per cent, and from Russian wool 6.6 per cent.

Anhydrous Wool Fat. Anhydrous wool fat is a light-yellowish, tenacious, unctuous mass, having a slight peculiar odor. It is insoluble in but miscible with large quantities of water, a property not encountered with any other wax. It is sparingly soluble in cold water, more soluble in hot alcohol, and readily soluble in ether and choloroform. The hydrous wool fat of U.S.P. grade is known in medicine as *adeps lanae hydrosus,* and the anhydrous as *adeps lanae.* Unless otherwise specified, *lanolin* is considered as the hydrous kind, and contains about 25 per cent of adsorbed moisture.

Physical and Chemical Characteristics of Wool Fat. Benedikt,[141] one of the early investigators, gave the melting point of wool fat (German) as 36 to 41°. The solidifying point is considerably lower, or about 30°. The index of refraction at 40° is 1.4781 to 1.4822, or 1.465 at 60° for Yorkshire grease. Wool wax rotates the plane of polarized light to the right $[\alpha]_D = +6.70$ at 35° (Walden). The chemical constants are as follows: acid value 0.5 upward, saponification value 82 to 127, iodine number (Wijs) 15 to 47), Reichert-Meissl number 4.7 to 6.9, acetyl value 23.3, glycerol content 0. Mixed fatty acids melt at 41.8°, and have iodine number 17, mol.

wt. 327.5. Mixed alcohols melt at 33.5°, having iodine number 26 to 36, acetyl value 144, mol. wt. 239.

Physical and Chemical Constants for Refined Wool Grease

Kind	Sp. Gr. at 15°	M. P. (°C)	Acid Value	Sapn. Value	Iodine No.	Unsapon. Matter (%)
Australian	0.940	——	15.5	112.7–113.3	16.5–29.5	——
German	0.932–0.944	37.5–40.0	0.5–4.5	84.2–98.3	15.3–17.6	35–45
Hungarian	——	——	5.6 max.	88.1–95.6	42.7–46.9	40–46.4
New Zealand	——	——	14.3	110.5–112.5	26.5	44
North American	0.932–0.945	38.0–40.0	——	82.0–127.0	15.0–29.0	39–44
Russian	——	——	13.9	94.2–95.9	—— ——	39
Yorkshire	0.943 (17°)	36.0–43.0	—	80.0–100.0	20.0–29.0	——
South American	——	——	13.2	96.7–98.9	—— ——	43.5
Wool Wax (fully refined)	0.904–0.919	48–55	18–22	139.0–140.0	35.0–56.0	32–42

Wool fat is difficult to saponify, and in making an assay the saponification value will increase appreciably as the time of saponification is lengthened. According to Utz,[141] on a sample of German wool fat the value increased in steps from 84.2 for ½ hour to 151.6 for 9 hours. This is attributed to the presence of *di-* and *trihydroxy acids* as well as the *monohydroxy acid.* The free acids in pure wool fat amount to less than 3 per cent, although on the raw grease they amount to 10 per cent or more. The total fatty acids is determined by first saponifying and then separating the fatty acids and working upon these. Heiduschka and Nier[57] obtained 62.7 per cent of fatty acids by this method, together with 32.8 per cent of unsaponifiable matter and 1.1 per cent of matter insoluble in ether. Fractionation of the fatty acids gave *cerotic acid* (m. 78°) and *lanoceric acid* (m. 102.5°). The cerotic acid was characterized by the preparation of the known derivatives and of the following esters: propyl, m. 65.5°; isopropyl, m. 75°; isobutyl, m. 65.5°; amyl, m. 63°. The lanoceric acid was transformed into the silver salt and ethyl ester, m. 78°. The unsaponifiable fraction contained *ceryl alcohol, isocholesterol,* m. 135–137°) and *cholesterol.* At least two other compounds were present, but carnaubyl alcohol could not be identified.

According to Kochs,[71] Kleinschmidt stated that pure lanolin contains 41.9 per cent of higher alcohols. The lower unsaturated alcohols are believed to be in a measure responsible for the emulsifying properties of wool fat. The mixed alcohols of wool fat have a melting point of 33.5° and a mean molecular weight of 239. The mixed fatty acids melt at 41.8° and have a mean molecular weight of 327.5.

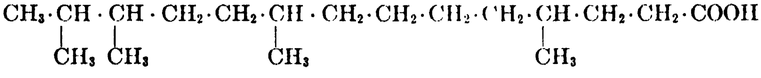
Lipson[89] extracted wool wax from the base of the fleece and found it to have an acid value of 4.94 and an iodine number of 33.5. He then attempted to separate the wax components by pouring a petroleum ether and benzene solvent through a column of alumina, with the result that it adsorbed 21 per cent of the wax, with the free fatty acids at the top, the free *cholesterol* (6 per cent) half-way down, and unidentified products, probably esters of higher fatty alcohols, at the bottom. Saponification of the unadsorbed filtrate gave *lanoceric acid* and *lanosterol,* with a small amount of *cholesterol* but no *agnosterol.*

Kuwata and Ishii,[78] in Japan, made an extensive investigation of the composition of wool fat, and found a considerable number of liquid saturated acids having iodine numbers less than 15. The solid acids were recrystallized repeatedly. Saturated C_{14}, C_{16}, C_{18}, C_{20} and C_{21} acids were separated, but they were not identical with the corresponding normal acids. They found new carboxylic acids of a so-called lano series: *lanomyristic* (m. 58.5 to 59.5°); *lanopalmitic* (m. 44.5 to 46.0°), *lanostearic* (m. 54.0 to 56.0°) *lanoarachidic* (m. 56.8 to 58.4°). A mixture of lanomyristic and normal myristic showed a definite melting-point depression. They also found *lanopalminic acid* (lanopalmic) ($C_{16}H_{32}O_3$, needles, m. 86.0 to 87.0°, $[\alpha]_D = +5.23$) and *lanoceric acid* ($C_{32}H_{64}O_4$). Another component is the ester of lanopalminic acid, isolated from wool wax separated from the scouring liquor of merino sheep wool. *Lanopalmic acid* ($C_{16}H_{32}O_3$) Kuwata found to be a stereoisomer of α-hydroxypalmitic acid. The methyl ester of lanopalmic acid melts at 45 to 46°; that of the α-hydroxypalmitic acid melts at 58 to 59°. Kuwata and Katuno[79] found two new alcohols in wool wax; one is termed *lano-octadecyl alcohol* (m. 42.0 to 43.0°) and the other *lanyl alcohol* (m. 79.5 to 80.0°). The latter appears to have the formula $C_{21}H_{40}(OH)_2$. In separating cholesterol from wool wax, methanol is suggested because of the low solubility of *isocholesterol* (now conceded to be a mixture of triterpene alcohols) in this solvent. From the hot methanol extract crude cholesterol wax precipitated on cooling, and pure crystals of *cholesterol* (m. 145.0 to 146.0°) were obtained by recrystallization from ethanol in ethyl acetate. Darmstädter and Lifschütz[34] as early as 1897 had isolated lanopalminic acid (m. 87 to 88°) and lanoceric (m. 103 to 105°), as well as the lower alcohols and cholesterol.

The chemical structure of *agnosterol* and *lanosterol* has always been uncertain, even to the extent that they are regarded by some students as triterpene alcohols rather than sterols, and all the more since they are not precipitated by digitonin, as are the sterols. Other students do not believe that they have the "picene" skeleton of 5 six-member rings of the triterpenes, but do have the "phenanthrene" skeleton of the 3 six-member rings plus a five-member ring common to the sterols (see sterols, p. 17).

Many of these uncertainties have been removed by the recent investigations of Ruzicka *et al.*[118b] Attempts to separate *isocholesterol* into its components by chromatographic analysis failed, and recourse was had to the older method of fractional distillation of the acetylated mixture. From the physical constants of the acetates and their saponification, Ruzicka was able to isolate *lanosterol* (m. 140 to 141°); *dihydrolanosterol* (m. 142.5 to 143.5°); *γ-lanosterol* (m. 156–157.5°); and *agnosterol* (m. 163.5 to 164.5°). But Ruzicka adds that "lanolin may contain other triterpene or steroid constituents" besides the aforesaid.

Little is yet known of the chemical structure of the lano-acids. They are believed to have forked-chain hydrocarbons. For example, *lanostearic acid* may have a structure of the following order:



$$CH_3\cdot\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CH_2\cdot CH_2\cdot\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CH_2\cdot CH_2\cdot CH_2\cdot CH_2\cdot\underset{\displaystyle CH_3}{\underset{|}{CH}}\cdot CH_2\cdot CH_2\cdot COOH$$

Chemical Composition of Neutral Anhydrous Wool Fat (Iodine No. 35)

Esters of Cholesterol and Fatty Alcohols with Fatty Acids: 73 per cent (Ratio 47.5% alcohols to 56.7% fatty acids):		
Lano acids:	lanomyristic	$C_{14}H_{28}O_2$
(7–7¼%)	lanopalmitic	$C_{16}H_{32}O_2$
Esters, m.p.	lanostearic	$C_{18}H_{36}O_2$
48–55°	lanoarachidic	$C_{20}H_{40}O_2$
	lanocerotic	$C_{26}H_{52}O_2$
Monohydroxy	lanopalminic	$C_{16}H_{32}O_3$ (D&L)
acids: (36–36½%)	lanoarachic	$C_{20}H_{40}O_3$ (30) (A&H)
	lanocerinic	$C_{30}H_{60}O_3$
Dihydroxy	lanoceric	$C_{30}H_{60}O_4$, m. 102.5° (D&L), and (or)
acids: (2–3%)		$C_{32}H_{64}O_4$, m. 103–104° (K&I)
Zoösterols:	cholesterol	$C_{27}H_{45}OH$, m. 145–148°
(10–11%)	7,8-dihydrocholesterol	$C_{27}H_{47}OH$, m. 128–129°
	oxycholesterol	$C_{27}H_{44}(OH)_2$
Unsaturated	decenyl	$C_{10}H_{19}OH$
alcohols: (8%)	hendecenyl	$C_{11}H_{21}OH$
	lanolin alcohol	$C_{12}H_{23}OH$ (of Marchetti)
	lano-octadecyl	$C_{18}H_{35}OH$, m. 42–43°
Saturated	cetyl	$C_{16}H_{33}OH$, m. 50°
alcohols: (8%)	carnaubyl	$C_{22}H_{45}OH$, m. 68–69°
Dihydric alcohols: (1.8%)	lanyl	$C_{21}H_{40}(OH)_2$, m. 78.5°
Free Fatty Acids (neutr. val. 170): 1 per cent		
	lanopalmic	$C_{16}H_{32}O_3$ (D&L)
	lanocerotic	$C_{26}H_{52}O_2$, m. 78°
Free Alcohols: 25 per cent		
ceryl alcohol		$C_{26}H_{53}OH$
triterpene	agnosterol	$C_{30}H_{47}OH$ (3 double bonds)
alcohols: 5%	γ-lanosterol	$C_{30}H_{49}OH$ (2 double bonds)
cholesterol 1%		
Lactone: less than 1 per cent		
lanocerin (lanoceri-lactone)		$C_{30}H_{58}O_3$, m. 88°
Mineral Matter (K_2O)*: less than 1 per cent*		
Hydrocarbons: 1 to 2 per cent		

Uses of Wool Waxes. Lanolin refiners in the United States have an output of somewhat over 75,000 pounds of lanolin per month. The larger part of the output is sold by refiners or dealers to the cosmetic trade. The refined grades of wax, or *lanolin*, are used as an ointment base, and as a superfatting agent for toilet soaps; they are very widely used in cosmetic creams. Lanolin is one of the few greasy substances that are absorbed by the skin and therefore finds use in skin softening, sunburn and "skin food" preparations. Lanolin, when properly blended with eucalyptus oil, makes an excellent pomade for the hair.

The poorer grades of wool grease are used in leather dressing as a finishing and softening agent. In England, wool grease has been found useful in the manufacture of paint, especially camouflage paint, and also in the production of anti-corrosive metal-coating compositions. For example, Howe's[64] composition comprises petrolatum 32, wool fat 32, mineral oil 15, and finely powdered mica 18. A composition of this kind may be applied to polished machinery or parts by brush. When used in soap, wool grease retards rancidity, increases lathering power and prevents crumbling otherwise due to dryness.

Wool Wax Alcohols. It is now possible to produce commercially *cholesterol* and *iso-cholesterol*, as well as *ceryl alcohol* from wool wax, or wool grease, by the Drekter and Conrad process.[37] In this process aqueous barium hydroxide is used as the saponifying agent for the raw stock, and iso-cholesterol is recovered by hot acetone treatment of the separated barium soaps. Cholesterol is extracted from the dried filtrate by means of hot methanol, the extract being distilled dry, and taken up with ethanol to crystallize out the cholesterol. Ceryl alcohol is recovered from the mother liquor by evaporating the latter to dryness with methanol or petroleum ether, and crystallizing out the ceryl alcohol.

Wool wax alcohols were introduced into the British Pharmacopœia in the 6th Addendum. They are obtainable from either raw wool grease or lanolin. The Wool Research Association[90] gives the following specifications for a select grade known as "Hartolan." Ash 0.2 to 0.3 per cent, soap 1.8 to 2.3 per cent, ester value 2.0 to 4.3, acid value 1.1 to 2.5, acetyl value 128 to 133, iodine number (Wijs) 44 to 45.2, m.p. 60 to 61°, *cholesterol* 28.2 to 34.1 per cent, iso-cholesterol 10.8 to 12.9 per cent. This grade has a mean molecular weight of 377, pH value 5.7, saponification value less than 8, flash point 393° F, fire point 474° F, viscosity at 200° F (Redwood No. 1) 232 seconds; unsaponifiable matter 96–98 per cent, specific rotation −11.8. The material has a brownish-yellow, wax-like structure, and is very brittle at 10° F. It does not become rancid.

Wool wax alcohols, according to Lower,[90] have the following applications: adhesive plasters, emulsifying agents, ointment bases, as artificial bile injections, suppositories, in leprosy treatments and antirachitic preparations, cosmetic preparations, biological creams, sun-tan preventives, hair bleaches, vitamin and hormone preparations. An example of the latter is estrogenic hormone cream.

Wool-Grease Soap. A solvent-extraction process for the removal of unsaponifiable matter from wool-grease soap has been patented by Smith and Campbell.[127a] The object of this is to assist in milling and to prevent the powdered soap from caking in storage. At a temperature of about 500° F the molten soap is run from the bottom of the soaping vessel in a thin layer onto a wide sheet-metal conveyor under which cold air is blown. The soap congeals rapidly and detaches itself, mainly in continuous lengths, from the end of the conveyor. In its tough plastic state, at about 200° F, it is taken by the ribboning or milling machine, which has three cast-iron rolls running at different speeds. The soap is fed from a hopper between two of the rolls, passing around the second roll and between it and the third roll, around which it passes and is removed by a scraper. If a serrated scraper is used, ribbons are formed.

The solvent extraction is done in a jacketed rotary-drier type of extractor vessel. A mixture of acetone with trichloroethane, carbon tetrachloride, or benzine is used. Methylethyl ketone and other ketones may be used in place of acetone. It is advisable to keep the solvent mixture down to a minimum gravity so that the soap ribbon will not float too near the surface.

SOLID MARINE ANIMAL WAXES

Spermaceti Wax

Spermaceti as officially defined[140] is a "peculiar, concrete, fatty substance, obtained from the head of the sperm whale, *Physeter macrocephalus*, Linné," and is in "white, somewhat translucent, slightly unctuous masses of a scaly, crystalline fracture and pearly lustre, with a very faint odor and a bland, mild taste. It becomes yellowish and rancid on long exposure to air."

Spermaceti is found in the head cavities and blubber, where it is dissolved in the sperm oil while the whale is living. After death, it concretes into a white spongy mass consisting of spermaceti mixed with oil. The sperm whale is the largest of the toothed whales, called also cacholots. It is from 60 to 80 feet in length, with an enormous head, 30 feet in circumference, in which there is a large hollow on the upper surface of the skull. This is filled with a peculiar fatty tissue. The oil contained in cells in this cavity, when refined, yields *spermaceti*; the *sperm oil* of commerce is derived principally from the thick covering of blubber, which completely envelops the body. When the spongy mass is removed from the head, the oil is allowed to separate by draining. The mass is boiled in a 2 to 3 per cent lye solution to clean it; it is then washed free from alkali, and the wax melted and moulded into cakes. Spermaceti also occurs in the bottle-nose whale *Balaena rostrata*[134] and in some other cetaceans, but not in the oil of whalebone whales.

The specific gravity of spermaceti is 0.938 to 0.944 at 25°, and 0.842 at 100°. Kebler[69] examined twenty samples of spermaceti and found a specific gravity of 0.905 to 0.945 at 15°. The German Pharmacopœia V limits the specific gravity to 0.940–0.945, which has been criticized as being too close. The refractive index at 70° is 1.4397 or thereabouts.

Properties of Spermaceti. It is interesting to note the various melting points recorded by early investigators for pure spermaceti: Saussure 47°, Chevreul 44°, Stenhous 41.6°, Wimmel 44–44.5°, Rüdorff 43.5 to 44.3°, Person 42.7°, Berzelius 44.7°, Liebig and Bolley 44 to 45°, Chateu and Schubarth 45°, Bunsen 47.7°, Pouillet and Müller 49°, and Dulk 50°.

The melting point of spermaceti should be within the range of 42 to 50° (107.6 to 122.0° F) according to the United States Pharmacopœia, and 46 to 50° (114.8 to 122.0° F) according to the British Pharmacopœia.[19] However, the usual commercial article melts at 42 to 44°. Hanzely[148] found the melting point of a fine specimen of spermaceti to be 45.8°. Spermaceti is insoluble in water and nearly so in cold ethanol. It is soluble in about 50 parts of boiling ethanol, also in ether, chloroform, ethylene dichloride, carbon disulfide, fixed and volatile oils, and only slightly soluble in cold petroleum benzine. It can be reduced to a fine powder by crushing with the aid of a little alcohol.

As found in commerce, spermaceti is not chemically pure,[139] as it contains a fixed oil and often a peculiar coloring principle. From these it is separated by boiling in alcohol, which on cooling deposits it in crystalline scales. When purified, it does not melt below 49°, is soluble in 40 parts of boiling alcohol of specific gravity 0.921 (Thenard), and is harder, more shining, and less unctuous than ordinary spermaceti. When re-crystallized from alcohol as just described, the purified *cetin* is obtained,[19] while the alcohol on evaporation deposits an impure sperm oil. The cetin which crystallizes out of the alcohol is essentially *cetyl palmitate* ($C_{15}H_{31}CO \cdot OC_{16}H_{33}$, m.wt. 480.83) that is, a compound of cetyl alcohol ($C_{16}H_{33}OH$) and palmitic acid ($C_{15}H_{31} \cdot COOH$).

There are small amounts of other esters with the cetin and also spermaceti esters containing the acids *stearic*, *myristic*, and *lauro-stearic*, and and the alcohol radicals corresponding to these acids. The alcohols were identified as early as 1854 by Heintz and termed *stethal* ($C_{18}H_{38}O$), *methal* ($C_{16}H_{34}O$), and *lethal* ($C_{12}H_{26}O$), now known as octadecyl, hexadecyl, and dodecyl alcohol, respectively. Common names are *stearyl*, *cetyl*, and *lauryl alcohol*, in the same order. Fatty acids obtained from spermaceti oil, when esterified with the correct amount of glycerol or glycol, produce diester products resembling japan wax.

The approximate chemical composition of pure spermaceti is given as follows:

Esters of Monobasic Acids: 98–98.5 per cent
Saturated: lauryl myristate, m. 32.0° (1–2%)
cetyl palmitate, m. 49.2° (90%)
lauryl stearate, m. 49.0° (3–4%)
cetyl stearate, m. 55.0° (1.1%)
Unsaturated: Unidentified (1–2%)

Free Monobasic Acids: 0.4 per cent
lauric acid $C_{12}H_{24}O_2$

Free Monhydric Alcohols: 1 to 1.5 per cent
cetyl $C_{16}H_{33}OH$, m. 50°
stearyl $C_{18}H_{37}OH$, m. 59°
oleyl $C_{18}H_{35}OH$ (traces)

Purity and Uses of Spermaceti. As spermaceti is occasionally adulterated with stearic acid or with paraffin or both, it is often necessary to test it for purity. Frerichs[46] recommends the following procedure: Heat one gram of the sample with 10 ml of aqueous ammonia in a test tube until the spermaceti is molten, shake well, cool and filter. The filtrate should yield no precipitate on addition of hydrochloric acid. One per cent of stearic acid, if present, gives a distinct cloudiness. Old samples, however, are likely to give a filtrate which is milky, when the test becomes indeterminate. In order to test for paraffin it is necessary to use absolute ethanol, the resultant solution being applied also to the determination of the acid content; 0.5 gram of spermaceti must be completely soluble in twenty five grams of boiling absolute ethanol. The solution should not be reddened by phenolphthalein solution (absence of alkali), and should require for reddening not more than 0.1 ml of 0.1N KOH. Admixture with stearic acid would become immediately apparent in the test for acidity, unless the sample were a very old one. The acid number should not exceed 2, the iodine number will fall between 0 and 6, and the ester number between 116 and 133. Dunlop[38] gives the acid value as 0 to 1.8; the saponification value 120.6 to 134.6; the iodine value of the highly purified spermaceti is 0, but values up to 9.3 (by Wijs' method) have been found, no doubt caused by the presence of sperm oil. The usual iodine number ranges from 3.0 to 5.9. The specific gravity of spermaceti may be determined rapidly by the usual hydrostatic method, with the aid of dilute ethanol, although accuracy of results by this method is open to question.

In medicine, spermaceti is used as a demulcent in irritations of the mucous membrane, but it has no remedial properties. An emulsion of this sort can be made by mixing spermaceti first with half its weight of olive oil, then with powdered gum arabic, and lastly with water. Spermaceti is used chiefly as a base for ointments, cerates, etc. Spermaceti Cerate (*Ceratum Cetacei*, U.S. Pharmacopœia, 1890) is made by melting together 10 parts of spermaceti and 35 parts of white beeswax, and then adding 55 parts of warmed olive oil. Spermaceti is used in cosmetics, in the finishing and lustering of linens, in *laundry wax*, and in special soaps and emulsifying agents.

Spermaceti is used to a limited extent in the manufacture of candles, and a little beeswax or other plastic wax is added to make the candles less crystalline and brittle. It is important to note that spermaceti is the wax used in the candle which defines our unit of candle power. The standard candle of Great Britain, which was also legalized in the United States, is one which weighs one-sixth of a pound and burns 120 grains of spermaceti per hour. In the manufacture of the English standard sperm candle it is prescribed by the Metropolitan Gas Referees in London that the wicks shall be made of three strands of cotton plaited together, each strand consisting of 18 threads. A number of other dimensional details are prescribed, and a careful description of the wax to be used in making the standard candle.

Cetyl Alcohol. Cetyl alcohol may be isolated[19] from spermaceti. When 10 parts of cetyl alcohol are used in conjunction with petrolatum 70, paraffin (m. 60°) 20, anhydrous lanolin 5, and the mixture ground with 100 parts of water., a good substitute for lanolin for many purposes is obtained. Chevruel in 1818 isolated cetyl alcohol by saponification of spermaceti, extracting the aqueous soap solution with petroleum ether. To secure a good yield it is best, according to Axelrad,[8] to prepare it from the calcium soap of spermaceti by distillation at a high heat. The wax is said to yield 40 to 45 per cent of cetyl alcohol by this method. In this process, 15 parts of the melted wax are mixed with 20 parts of lime containing 5 per cent of water, heated and stirred for six hours, the water being distilled at 100°, and then the temperature allowed to rise to 340° when the cetyl alcohol distills off in the form of oily drops which solidify to a white mass (m. 49.5°) on cooling. It is claimed that the distillation can also be conducted *in vacuo* at a lower temperature. There is a fairly large commercial demand for cetyl alcohol.

Cetyl esters can be produced from sperm oil by hydrogenating the oil,[118] and separating the triglycerides by mild saponification in the cold. The product is a diaphanous, crystalline, odorless and tasteless mass closely resembling spermaceti and containing 75 to 85 per cent of compound *cetyl esters*, 2 to 4 per cent of *triglycerides* and 10 to 20 per cent of *cetyl alcohol.* It is said to have value in the production of cosmetics *e.g.*, lipstick. Under the name of *cetiol* this hydrogenated form of sperm oil or spermaceti is used to replace mineral oil in a superior non-foaming type of shampoo.

LIQUID ANIMAL WAXES

Liquid waxes are those which are liquid at ordinary room temperature. They are on the boundary line between the vegetable oils and solid waxes in many of their physical and chemical constants, but differ from fatty oils since they are virtually free from glycerides. They consist mainly of esters of unsaturated alcohols with unsaturated fatty acids, in which respect they resemble the true waxes, except for being liquid. They are less dense than glycerides and do not thicken or dry on exposure to air—a highly advantageous property; but they yield solid elaidins on treatment with nitrous acid. The group includes marine oils, a vegetable oil, and a bird oil, as will be mentioned.

In the marine animal waxes certain saturated and unsaturated alcohols containing 16, 18, or 20 carbon atoms per alcohol, replace the glycerol found in fats, and hence they are well termed "liquid waxes." On cooling they deposit material of wax-like properties consisting largely of *cetyl palmitate.* Spermaceti is formed in this manner. In the separation of spermaceti the yield is only ten to fifteen per cent, and much of the solid wax remains dissolved in the liquid constitutents.

Sources of Liquid Waxes

Arctic sperm oil is a liquid wax from the bottlenose whale, *Hyperoodon rostratus*; it is also called *bottlenose oil* and *doegling oil.* It has very similar characteristics to sperm blubber oil of the true sperm whale or cachalot. *Dolphin oil* is a mixture of liquid wax and fat from the dolphin, *Delphinus delphia. Sperm oil* (sperm-head oil) is a pale-colored liquid wax from the large cavity in the head of the sperm whale, *Physeter macrocephalus*, L., and is also known as *spermaceti oil* and *cachalot oil. Jojoba oil* is a liquid wax from the seeds of the plant, *Simmondsia californica* (see p. 172).

Mutton bird oil is a liquid wax from the stomach of the mutton bird, a petrel known as *Aestrelata lessoni.* To quote L. Wilson Greene: "Why liquid waxes occur in two species of whales, two of fish, one bird, and the seeds of a plant is an intriguing question, especially when we consider that the lipoids of other whales, fish, birds, and plant seeds are mostly fats."

Mutton Bird Oil

Smith[127] stated that mutton bird oil was the first bird oil to be put on the market. The output (from New Zealand and Tasmania) is small and is not likely to be of commercial importance. The oil, which is found in the bird's stomach, has a ruby-red color and a not unpleasant fishy smell.

The sample of Smith and two others obtained years later by Evers and Foster[40] are described as follows:

	Smith	Tasmania (E. & F.)	New Zealand (E. & F.)
Condition	liquid	liquid	soft solid
Sp. Gr. 15.5°/15.5°	0.8819–0.8858	0.8835	0.9179 (20°/15.5°)
Refractive Index at 20°	——	1.4712	1.4713
Saponification Number	125.9	125.9	200.0
Iodine Number (Wijs)	71.0	132.0	99.5
Acid Number	——	5.7	6.8
Unsaponifiable	36.88%	31.1%	0.98%
Melting Point	30.5–31.5°	32°	——
Titer	29.4	——	——
Ether-insoluble Bromides (Gemmel test)	——	10.4%	0

It is believed that the oil might be of value as a substitute for cod liver oil, but little is known of its therapeutic value. The New Zealand oil of Evers and Foster corresponds more to the body fat of the bird as described by Smith, and which contains little unsaponifiable matter.

Sperm Oil

Sperm oil from the blubber and the cavities in the head of the sperm whale, *Physeter macrocephalus*, L., consists of esters of fatty acids and fatty alcohols, a large proportion of which are either unsaturated in the alcohol radical or in the fatty acid radical, or in both. The blubber or body oil is the far more unsaturated of the two, and it is the head oil, or the more saturated, that deposits on cooling the cetyl palmitate or spermaceti wax.

The oil prepared exclusively from the body blubber is orange-yellow in color, and will deposit a considerable amount of crystalline solid with the following constants as determined by Toyama: 20°/4° 0.8806; 30°/4° 0.8733; $n \frac{30^\circ}{\mathrm{D}}$ 1.4620; acid value 1.24; saponification value 131.6; iodine number 82.4; unsaponifiable matter 36.40 per cent and fatty acids 64.13 per cent. The fatty acids are orange-yellow in color and liquid at ordinary temperature; d 20°/4° 0.8918; 30°/4° 0.8847; $n \frac{20^\circ}{\mathrm{D}}$ 1.4602, $n \frac{30^\circ}{\mathrm{D}}$ 1.4564; neutral value 199.2; saponification value 201.8· iodine number 87.4 and ether-insoluble bromides 5.55 per cent. The fatty acids consist of about 10 per cent saturated and 90 per cent unsaturated acids. *Myristic, palmitic, stearic* acids and a little *arachidic acid* form the saturated acids, the palmitic acid being preponderant. The acids of the oleic series contain *zoömaric* and *oleic acid,* an acid $C_{20}H_{38}O_2$, and *cetoleic acid.* An acid ($C_{14}H_{28}O_2$) is also present in small quantity. The unsaponifiable matter (36.4 per cent) consists chiefly of *oleyl alcohol, cetyl alcohol* and *octadecanol,* of which oleyl alcohol (octadecenol) is preponderant. *Cholesterol* is also present to the extent of 0.44 per cent.

Martin[97] gives the specific gravity of the body oil as 0.880 to 0.883 at 15°; saponification value 123–133; iodine number 81–84; Reichert-Meissl value 0.60; fatty acids 60–64 per cent, alcohols 37–41 per cent, Maumene test 45–51. The high iodine number is indicative of the preponderance of unsaturated esters.

Hilditch[62] directs attention to distinct differences in the chemical composition of sperm-head oil and sperm-blubber oil. According to Hilditch, the head oil has a relatively high content of lauric and myristic acids; the blubber oil is less saturated in its alcoholic and acidic components.

The following is the approximate composition of a typical *sperm head oil* having an iodine number of 61.8:

Oil	Per cent
Myristyl caprate	4.5
Cetyl laurate	20.0
Hexadecenyl lauroleate	7.0
Oleyl myristate	13.0
Oleyl myristoleate	18.0
Cetyl palmitate	9.0
Hexadecenyl palmitoleate	3.0
Oleyl oleate	11.0
Stearyl stearate	2.5
Eicosenyl eicosenate	7.0
Eicosenyl eicosdienoleate	2.0
Undetermined	7.0

In the undetermined is a small amount of cholesterins, and traces of physeteryl alcohol (tetradecenol). The hexadecenyl alcohol referred to is *zoömaryl alcohol.* There is also present a small amount of *d-glyceryl ethers.*

Peculiarly, the unsaturated alcohol portion of the esters is as susceptible to hydrogenation as the unsaturated acidic part of the molecule, whence the unsaturated alcohols are convertible to cetyl, octadeyl, and eicosyl (C_{20}) alcohols. Hence *hydrogenated sperm oil* is capable of producing far higher yields of *spermaceti wax* of higher melting point and harder than commercial pressed spermaceti. The sperm oils are free from linoleic acid ($C_{18}H_{32}O_2$), which is found in ordinary whale oils to the extent of about 9 per cent, and in a still larger proportion in some fish oils.

Chemistry of Sperm Oil. The chemistry of the unsaponifiable portion of sperm oil is not so well known for the lesser components. Sperm and arctic sperm (doegling) oils consist largely of oleyl alcohol ($C_{18}H_{35}OH$), but contain small amounts of alcohols known as batyl, selachyl, and chimyl. They appear to be of the nature of glyceryl anhydrides. The study of the latter is best made from the unsaponifiable portion of the liver oils obtained from certain species of sharks and rays. Toyama[135], and more recently Baer and Fischer[9], have studied the configuration of the natural batyl, chimyl and selachyl alcohols. The relation between them may be explained in the following simple manner even though they cannot be thus prepared:

$C_{18}H_{36}O$	+	$C_3H_8O_3$	=	$C_{21}H_{42}O_3$	+	H_2O
oleyl alcohol		*glycerol*		*selachyl alcohol*		*water*
$C_{18}H_{38}O$	+	$C_3H_8O_3$	=	$C_{21}H_{44}O_3$	+	H_2O
stearyl alcohol		*glycerol*		*batyl alcohol*		*water*
$C_{16}H_{34}O$	+	$C_3H_8O_3$	=	$C_{19}H_{40}O_3$	+	H_2O
cetyl alcohol		*glycerol*		*chimyl alcohol*		*water*

Batyl alcohol has been found to be identical with *d*-α-octadecyl glycerol (m. 71–72°); *chimyl alcohol* is identical with *d*-α-hexadecyl glycerol (m. 62.5–63.5°); *selachyl alcohol,* according to Baer and Fischer,[9] can also be assigned to the *d*- series, because it is reducible to batyl alcohol. Selachyl alcohol is also referred to as α-oleyl glyceryl ether, and chimyl alcohol as α-cetyl glyceryl ether. Selachyl alcohol is found in the liquid portion of the unsaponifiable; the other two alcohols are solid, the chimyl alcohol predominating. The hydrogenated unsaponifiable melts at 64 to 68.5°. Hydrogenated sperm oil contains *octadecylic alcohol* (stearyl alcohol) and also batyl and chimyl alcohols. It is a wax-like product which has considerable value for cosmetics and similar purposes.

The glyceryl ethers were shown by André to occupy a position between the glycerides and waxes:

$(R\cdot CO\cdot O)_3\cdot C_3H_5$	$(RCO\cdot O_2)_2\cdot C_3H_5(OR')$	$R\cdot CO\cdot OR'$
glyceride	*glyceryl ethers*	*waxes*

The following tabulation shows the differences between head oil and blubber oil.

Alcohol	Head Oil (%)	Blubber Oil (%)
myristyl, $C_{14}H_{30}O$	—	2.1
physeteryl, $C_{14}H_{28}O$	—	traces
cetyl, $C_{16}H_{34}O$	50	21.1
zoömaryl, $C_{16}H_{32}O$	10–12	7.4
stearyl, $C_{18}H_{38}O$	10–12	5.2
oleyl, $C_{18}H_{36}O$	25	49.7
eicosenyl (eicosenol) $C_{20}H_{40}O$	3–5	6.1
eicosdienol $C_{20}H_{38}O$	—	2.1
undetermined (glyceryl ethers)	—	6.5
Acid		
capric, $C_{10}H_{20}O_2$	4	—
lauric, $C_{12}H_{24}O_2$	18	1
lauroleic, $C_{12}H_{22}O_2$	6	—
myristic, $C_{14}H_{28}O_2$	12	3
myristoleic, $C_{14}H_{26}O_2$	16	3
palmitic, $C_{16}H_{32}O_2$	8	8
palmitoleic, $C_{16}H_{30}O_2$	2	24
oleic, $C_{18}H_{34}O_2$	10	35
$C_{20}H_{40-x}O_2$	6	10–12
$C_{22}H_{44-x}O_2$	—	10–12

Commercial Sperm Oil. The sperm oils have been graded by the oil refineries as *winter sperm oil*, congealing below 38° F, the yield being about 75 per cent from the crude; *spring sperm oil*, congealing at 50° to 60° F, 9 per cent yield; *taut-pressed oil*, melting at 90 to 95° F, 5 per cent yield; and *crude spermaceti*, melting at 110 to 115° F, 11 per cent yield. Sperm oil is a thin yellow liquid, and when of good quality is nearly free from odor. Allen gives its specific gravity as ranging between 0.875 and 0.884 at 15.5°. Sperm oil stands at 44° to 46° on the Casartelli hydrometer. This hydrometer used by dealers shows water at 0 and rapeseed oil at 28°. Southern whale oil is said to stand 24° on the same scale. The flash point must exceed 225°.

Sperm oil on saponification yields oleate and monohydric alcohols, which is not true of ordinary oils; hence sperm oil is classified as a *liquid wax*. Sperm oil yields 39.2 per cent of wax alcohols, and 1.3 per cent of glycerol on saponification, cachalot 41.2 to 44.3 per cent of wax alcohols, and Arctic sperm 38.0 to 39.2 per cent of wax alcohols. Sperm oil yields 60 to 63 per cent of insoluble fatty acids. Other oils yield a considerably higher amount, and 10 to 12 per cent glycerol.

Sperm oil is preferable to any other fixed oil for lubricating the spindles of cotton and woolen mills, and delicate mechanisms like watches, owing to its limpidity and freedom from tendency to "gum" and become rancid. It retains its viscosity at high temperatures. It is used to some extent as a burning oil in lamps, in hardening steel, in the manufacture of specialty soaps, in dressing leather, and as a drawing lubricant. *Bottlenose oil* and *Arctic sperm oil* are used for substantially the same purposes.

When sperm oil is mixed with mineral lubricating oil (*e.g.*, 1 to 10) and subjected to a silent electric discharge in a glass tube apparatus there results a very pronounced increase in viscosity and greatly improved lubricating properties in engines. The polymerized liquid wax constituent of the sperm oil is soluble in the hydrocarbon oils, and according to Russell[118a] suitable formulations can be arrived at that will greatly increase the viscosities in the range of 540 to 2000 seconds. Saybolt at 210° F.

Doegling or Bottlenose Oil

Doegling or bottlenose oil is a fluid very similar to sperm oil, particularly blubber sperm oil, with almost identical analytical constants. It can be distinguished from sperm oil by its taste. It is lower priced than sperm oil on account of its having a slight tendency to "gum." The constants for doegling oil have been given as : sp. gr. 0.875–.890, acid value 0.1–0.4, saponification value 123–144, iodine number 81.3–84.0, unsaponifiable 32–41 per cent.

hale Oils

The principal source of supply of marine oil is the whale. Whale oil, unlike sperm oil, contains little of the waxy constituents. In whaling today the blue whale is sought, as its yield of product equals that of the finbacks, two and a half humpbacks, or six sei-whales. These whales are all of the rorqual family, and differ from the sperm whales, bottle-nosed whales, and dolphins. German whaling aims are concerned largely with the great blue whale, finback, and humpback, which provide food fats, specifically whale-oil margarine. Such fats are also of prime importance in the Scandinavian countries and elsewhere. American consumption of the oil, on the other hand, has thus far related chiefly to the manufacture of soap. High-grade tallows can be made by partial hydrogenation of whale oil, and complete hydrogenation results in a high-melting, more wax-like product. There are 24 floating factories and 281 whale-catchers operating in Antarctic waters, producing half a million tons of oil—a far greater output than that of the Arctic. The sperm whale is one of a family order largely confined to tropical waters, but stragglers reach both polar seas. *Sperm oil* is everywhere mixed with spermaceti, but a preponderately large amount of spermaceti is obtained from the case occupying most of the snout of its enormous head, and yielding almost 500 gallons of mixed sperm oil and spermaceti. The production of sperm oil is insignificant in tonnage when compared with that of common whale oil.

Part III: Waxes from Plants

The Ecology of the Plant Waxes

The outer wall of the epidermis of an adult plant leaf is thickened by the deposition of *cutin*, a fatty substance highly impermeable to water; usually the cutinized portion forms a continuous yellowish coat. Without cutin the thin epidermis would be permeable because of its cellulosic composition. In the grasses and the rushes, silica is deposited in the cell walls in addition to cutin. Plants of dry areas, such as deserts, dry rocks, and dry sands, are known as xerophytes, and their leaves are highly cutinized. Particularly is this true of the evergreen xerophytes, such as conifers, ericads (revolute type, *i.e.*, with edges curved under), and some of the broad-leaved trees, *e.g.*, live oak and olive. The leaves of many of the alpine and arctic plants and of the peat are bogs heavily cutinized; so also are those of the mesophytic evergreens (plants of fairly moist soil) such as the yew and the hemlock. It is believed that the heavy cutinization of the mesophytes of the dwarf plants like mountain hemlock (*Tsuga mertensiana*, Carr.) may be due to limited root systems. Many leaves of these scraggy (Krumnholz) plants appear "glaucous," and have a bluish-gray film of wax, sometimes known as "bloom," which is removed by rubbing. Such waxy cutin retards the egress of water from leaves, and greatly reduces the transpiration. Sometimes these wax deposits are thick, forming a brittle crust, as in certain fleshy perennial herbs (*Sempervivum spp.*) and in the wax palms, or layers of vertical rods, as in sugar cane.

De Bary[14] distinguished four characters of wax coating:

(1) Continuous layers or incrustations of wax, *e.g.*, on the leaves and stems of purslane, *Portulaca spp.*; leaves of fuchsia, *Zauschneria spp.*; yew, *Taxus spp.*; the stems of the wax palms, *Ceroxylon spp.*, etc.

(2) Coatings composed of multitudes of minute rods placed vertically side by side upon the cuticle, *e.g.*, on the stems of the sugar cane; *Coix lachryma*, L. (Job's tears grass), and some other grasses.

(3) Coatings of minute rounded grains in a single layer, *e.g.*, on the leaves of the cabbage, *Brassica spp.*; onion, *Allium spp.*; tulip, *Tulipa spp.*; clove pink, *Dianthus caryophyllus*, L., etc.

(4) Coatings of minute needles or grains irregularly covering the surface with several layers, *e.g.*, on the leaves of the blue gum-tree, *Eucalyptus globulus*, Labill; rye, *Secale spp.*, etc.

As with hairs, but not with cutin, wax coats are best developed on the under-leaf surface where the stomata (pores) are the most abundant, as in this location it is the more effective in checking transpiration. Wax is not the only means, however, as nature provides resin particularly where there is intense heat from the sun's rays, *e.g.*, on the leaves of the creosote bush, *Covillea tridentata*, Vail., and on many other desert xerophyles.

Wax may form an incrustation over the whole leaf, as in the bog bilberry, *Vaccinium uliginosum*, L., which grows on the summits of mountains in New England and the Adirondacks; or only on the stomatiferous lower face, as in the bog rosemary, *Andromeda polifolia*, L., an evergreen shrub; the small cranberry, *Vaccinium oxycoccus*, L., a creeping evergreen vine; the mealy primrose, *Primula farinosa*, L., a species of willow, *Salix groenlandica*; and the carnation grass, *Carex panicea*, L. Wax is found excreted over the surface of certain hydrophytes, to protect them from saltiness, as in the North American swamp-plants, *Acer rubrum*, L., red or swamp maple, and *Persea pubescens*, Sarg., swamp bay, and others.

The degree to which wax on cuticle surfaces of the leaves, stems and fruits, depresses transpiration was experimentally established by Tschirch and Haberlandt[146] in 1882. Usually the coating produced is only a thin one, but to take an opposite case, the hyssop of the Scripture, *Capparis spinosa*, L., at the commencement of the dry season in the Egyptian desert, excretes a very thick layer of wax over the whole leaf surface that completely prevents transpiration. The thickness of the heavier wax coatings may range from 1 mm as in *Sarcocalla spp.*, in South Africa to 5 mm in *Ceroxylon spp.* in South America. Bloom-covered leaves usually have no sharp teeth at their margins, and possess at most rounded teeth provided with hydathodes. As wax prevents water from wetting leaves, it protects ombrophilous foliage from rain.

A group of xerophytic plants known as halophytes, since they are associated with salt water in maritime areas, have a glaucous, or mat blue-green surface, on their leaves due to the wax coating, *e.g.*, the sea pea, *Lathyrus maritimus*, L.; the sea holly, *Eryngium maritinum*, L.; the sea lungwort, *Mertensia maritima*, L.; yellow sea poppy, *Glaucium flavum*, Crantz; the *Crambe maritima*, and *Spinifex squarrosus*. Included in these dune plants is *Elymus arenarius* which has broad leaves glaucous with wax, like those of the *Triticum junceum*.

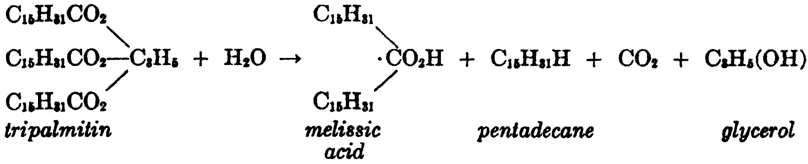
In the fruits, deposits of wax in the cutinized layers of the epidermis cause water to flow over the cuticle without being absorbed. This is the case in such fruits as plums and grapes, on which the wax covering forms the so-called bloom; it may consist of grains, small rods, or crusts.

Formation of Wax in Arid Plants. The plants which produce the greatest amount of wax for their weight are those found in hot or tropical climates, particularly in arid regions. Waxes from such plants have an appreciable amount of hydrocarbons in their chemical composition; for example, candelilla wax contains nearly 50 per cent of hydrocarbons. Some plants in the temperate zones produce waxy material in their fruits, but this is of a fatty nature, largely if not wholly consisting of one or more triglycerides, for example, the wax of the myrtle berry.

In the arid plants, glycerides in the form of fat or oil, built up by a reductive process and carboxylation, apparently are transformed into new chemical entities, such as high molecular weight alcohols, acids, and hydrocarbons. These processes are the result of the metabolic changes occurring daily according to the presence or absence of light action, warmth, and moisture, and the nature of the plant species. The processes of nature involve carboxylation, reduction, hydrolysis, oxidation, decarboxylation, and the photochemical reaction between hydrocarbons and hydroxy acids to form esters, containing an even number of carbon atoms, and water.

For example, if *tripalmitin* and *palmityl alcohol* are taken as representative constituents of the fat, or oil, found in the pollen or tissues of plants, we might expect to obtain *melissic acid*, *pentadecane* and glycerol by hydrolysis and decarboxylation of this glyceride. When sunlight is absent, the glycerol so formed would tend to retain moisture, but the arid condition of the soil probably withdraws the glycerin to the plant roots, and hastens the formation of more wax acids and hydrocarbons in the exposed portions of the plant, thus reducing oily or fatty constituents to a minimum

The decarboxylation of natural vegetable fats and oils proceeds in stages. With *tripalmitin* it probably proceeds to a secondary stage with the elimination of just two carboxyl groups, as shown in the reaction:



$$\begin{array}{l}C_{15}H_{31}CO_2\diagdown\\ C_{15}H_{31}CO_2{-}C_3H_5\\ C_{15}H_{31}CO_2\diagup\end{array} + H_2O \rightarrow \begin{array}{l}C_{15}H_{31}\diagdown\\ \quad\cdot CO_2H\\ C_{15}H_{31}\diagup\end{array} + C_{15}H_{31}H + CO_2 + C_3H_5(OH)_3$$

Palmityl alcohol, accompanying the glyceride, would assimilate the CO_2 to produce *hydroxymargaric acid* thus:

$$\underset{\textit{palmityl alcohol}}{C_{16}H_{33}\cdot OH} + CO_2 \rightarrow \underset{\textit{hydroxymargaric acid}}{C_{16}H_{33}O\cdot CO_2H}$$

Pentadecane arising from the decarboxylation then reacts with the hydroxy acid to produce *palmityl palmitate,* which on subsequent decarboxylation yields *hentriacontane*:

$$\underset{\textit{pentadecane}}{C_{15}H_{31}H} + \underset{\textit{hydroxymargaric acid}}{HO\cdot CO_2\cdot C_{16}H_{33}} \rightarrow \underset{\textit{palmityl palmitate}}{C_{15}H_{31}\cdot CO_2\cdot C_{16}H_{33}} + H_2O$$

$$\underset{\textit{palmityl palmitate}}{C_{15}H_{31}CO_2\cdot C_{16}H_{33}} - CO_2 \rightarrow \underset{\textit{hentriacontane}}{C_{31}H_{63}\cdot H}$$

In metabolism it is possible to double up on the molecular weight of the alcoholic group of an ester in the following synthesis:

$$\underset{\textit{hentriacontane}}{C_{31}H_{63}H} + \underset{\textit{hydroxymargaric acid}}{HO\cdot CO_2\cdot C_{16}H_{33}} \rightarrow \underset{\textit{melissyl margarate}}{C_{16}H_{33}\cdot CO_2\cdot C_{31}H_{63}} + H_2O$$

Melissyl margarate is a constituent of *Ghedda wax,* and it is uncertain whether the ester naturally occurs in the plant pollen, and is extracted by the bee, or whether the bee produces it through the enzymes in its digestive tract.

WAXES FROM PLANT LEAVES AND STEMS

Classification

Waxes from the leaves and stems of plants may be grouped in the following manner for the sake of convenience.

(1) Waxes of palms. The wax is generally more abundant on the leaves than on other parts of the plant. *E.g., Copernicia cerifera,* Mart., which provides carnauba wax.

(2) Waxes of herbs and shrubs. The wax is often distributed over

the whole plant as well as on the leaves. *E.g.*, *Pedilanthus pavonis*, Boiss., which is a source of candelilla wax.

(3) Waxes of grasses and sedges. The wax covering is usually heavier on the stem. *E.g.*, *Saccharum officinarum*, L., which is the source of sugar-cane wax.

(4) Waxes of broad-leaf trees. The leaves contain only minute amounts of wax.

(5) Waxes of narrow-leaf trees. The leaves of the conifers yield essential oils from which wax is often recoverable.

Group (3) covers the plant order *Graminales*. This order has two families, the grasses (*Gramineæ*) and the sedges (*Cyperaceæ*). The plants of the grass family generally have cylindrical hollow culms with swollen nodes, which contain a considerable amount of wax. Some species of *Gramineæ* are very tall and have woody, siliceous stems, *e.g.*, the bamboos of the tropics. The cereal plants are included in the grasses. Sedges are relatively unimportant as wax bearings plants.

In group (4) the broad leaves of the maple, beech, and oak when mature contain minute quantities of wax which may be extracted with ether. In the leaves of the maple and beech, *cerotic acid* has been isolated, and also *phytosterols* differing in their crystalline form. Wax is recoverable from essential oils produced from certain broadleaf evergreen species of *Eucalyptus* and the like.

(1) *Palm Tree Waxes*

Carnauba Wax

Carnauba wax is obtained from the leaves of a species of an American genus of palm designated as *Copernicia* (or *Copernica*) *cerifera*, Martius, named in honor of Copernicus. The name *carnauba* is believed to be a corruption of the Tupi *carnahyba*, compounded from *caraná* or *carandá*, meaning scaly, thick-skinned or -barked, and *yba*, meaning tree or palm.

The carnauba is a straight-trunked palm of slow growth, attaining an average height of 25 to 33 feet, but seldom more than 40 to 50 feet even after 50 years of growth. The bark is scaly, rough, and thick, and the leaves grow out from yard-long petioles in wide serried fan shapes. The tree reproduces prolifically. The ovaloid fruit resembles a hazel nut, and when ripe it falls to the ground, where dense clumps of shoots spring up, some of which survive to form saplings.

The flowers are monoecious, very small and numerous, and grow from an appendix in the axils of the leaves. During the dry months the leaves and petioles exude a wax through the pores. Nature provides this wax to prevent excessive evaporation of water from the plant. The summer sun from July to December seems to stimulate the production of wax,

FIGURE 4. *Copernicia cerifera*, Mart. Well developed carnauba palms on dry ground which is only subject to periodic floods. State of Parahyba, Brazil.

although the available wax may even increase with the occasional winter rains.

The natural habitat of this Brazilian wax palm extends from Bahia, near the banks of the São Francisco River, to the distant Amazon; that is, in the semi-arid Brazilian Northeast. The states which are the principal sources of carnauba wax are Ceará, Piauhy, Rio Grande do Norte, and Mãranhao. There are two varieties of the carnauba palm which the

FIGURE 5. A grove of carnauba palms along the river bed of the Parnahyba, Brazil. The carnauba palm prefers to grow along the banks of rivers and lakes.

natives of the Northeast distinguish as white and red. A black variety also exists. The palms have no master root; the roots stretch out over the surface of the ground in search of moisture. The carnauba palm prefers to grow along the banks of rivers and lakes, but it is also found in small isolated groves from the damp lowlands along the coast to the forests of the interior.

Economic Value of the Carnauba Palm. The carnauba palm is of great value to the *sertanejos*,[145] the inhabitants of these flat semi-arid lands, and the historical evolution of the Brazilian *setao* is closely allied with this rough-barked, fan-topped palm, which supplies him not only food, drink, and a cash crop, but also fibers for clothing, timber for housebuilding, and even his light. The timber is hard and useful for laths to take plaster, pilings which will resist the brackish waters, bridges, fences, and excellent furniture. It is almost impervious to the attack of insects. The bark may be used as firewood. The leaves are utilized for window and door shades. There is food value in the tender end shoots and from them can also be made wine, vinegar, and a saccharine substance. The bunches of fruit, rust-colored when ripe and dried, may be crushed for cooking oil. The roasted and pulverized fruit may be brewed to a coffee-like drink. A starchy flour like manioc flour can be prepared from the medullary pith, or the pith may be fermented to an alcoholic drink. A medicinal is extracted from the roots. The saplings and tender shoots are fed to cattle in case of drought.

The important hat industry of Ceará uses the superior quality of carnauba leaves, turning them into hats similar to Panamas which are shipped everywhere in Brazil. The natives sleep in hammocks made from the fibers. Fine cordage, nets, baskets, mats, and curtains are also woven from the fibers. The fiber from the petiole is made into brooms and brushes. Although only the wax has given the carnauba palm universal renown, it can be readily understood that there is no plant in existence that is of greater value to the Brazilian native. For light he melts a small portion of tallow with the wax, and solidifies the melt around a cotton wick to form a candle. The carnauba candle, however, is not the best source of illumination!

Harvesting the Carnauba Leaves. The cutting of the leaves and sprouts generally takes place during the dry months of the year, usually between September and December or January. The production of carnauba wax has been described by Walmsley.[145] Workers known as "moradores," a class of herdsmen, contract with, or are hired by, the proprietor to remove the wax from the leaves of the stand of palm trees, and to melt it for shipment. The "moradores" are also sometimes squatters on the property, and receive a share in the profits of the harvest on the share-cropping principle. They chop through the stems with a *foice,* a curved sickle-like knife fastened to the end of a long pole. As the leaves fall to the ground the long stems are slashed off and then the leaves are carefully transported to a central terrace for drying in the sun. There are two cuttings (sixty days apart) per tree in a normal year, but there is a yield of only eight to twelve leaves per cutting. Only mature leaves are harvested. The sun-drying takes from three to five days. A suitable drying terrace consists of a tiled or cement floor 10 to 14 feet square surrounded by an unroofed wall 2½ feet high. The wax dust is very light and flour-like and is easily dispersed by a slight gust of wind.

From the drying terraces the leaves, with their wax loosened by sun-drying, must be transported with the greatest of care to the shed for trenching, threshing, and beating. The shed is about 15 feet long and 12 feet wide, and so constructed as to prevent any gust of air passing through it. The operators work with the door closed, and trench leaves over tooth-like blades fixed upright in a block of wood. The idea is to cut through the fiber, thus splitting the wax-containing ribs apart and opening up the webs. The leaf is then ripped apart by hand to loosen the wax, and the leaves in small bunches are beaten against a sort of wooden sawhorse to remove all the wax dust. The spent leaves are thrown out of the hut. Afterwards the dust is swept into small bins or closely woven bags preparatory to melting. The walls and roof are also brushed to remove wax powder. Three workers can handle about 4000 leaves a day.

Preparation of Carnauba Wax. Melting is carried out in the melting room in either clay vessels or open iron pots, directly over a wood or charcoal fire. The wax is also often bagged in powdered form and shipped to the coast. In the native processing of carnauba wax, the flour is sometimes melted down in an old 5-gallon petrol can from which the top has been removed. A full 5-gallon can of powder will melt down to less than a quart of molten wax. The wax is slowly melted over a fire, being stirred constantly during the operation, and then strained through a thick cloth. The procedure of harvesting and wax recovery here described is commonly used in the State of Ceará. In Piauhy, which is the only other very large producing state, the practice is a little different, because of the danger of expected rain. The green leaves are slit by long sharp knives into fine shreds which remain attached to the butt end of the leaf, and the leaves are sun-dried for only one day.

Various modifications in the recovery and melting procedure are necessary to obtain the classified grades of carnauba wax, as they are known commercially. A brief description will be given of these grades. About 30 per cent of the total production is the melt from the *olho* leaf—the young, yellow, unopened leaf that grows upward from the "cabbage ball," at the center of the palm. The powder is melted and the "top portion" drained into little pans or saucers. This wax is known as *cera flor* or *flor fina*. It represents only one per cent of the total production of carnauba wax and is the most expensive. In straining the bulk of the molten wax of the "olho" leaf through cheesecloth *primeira* or *amarella primiera* (Yellow No. 1) is formed, which has a somewhat murky, pale yellow color, contrasted to the clean and more straw-like côlor of *flor fina*. *Mediana clara* (Yellow No. 2) is quite similar, but grayish in color. Inferior grades are *mediana roxa* and *cauhype*, which represent the wax recovered from the residues, and are consumed locally. They are gray and grayish-black in color.

Approximately 70 per cent of the output is obtained from the *palha* grades, which are produced from the *palha* leaf, *i.e.*, the fan-spread leaf harvested from the same tree as the *olho* leaf. These *palha* waxes are more greenish in color, varying from a pale greenish-yellow, characteristic of the large mature leaves, to a pale gray-green; the inferior grades are gray, dark gray, or even black. The *palha* wax is known as *gordurosa*—meaning waxy—or as "north country wax." The melted wax is drained into petrol cans, after straining through cotton or burlap, and through beaten fibers or leaves. If the chalky grade known as *arenosa*—meaning chalky—is desired, it is made by adding a cup of sour salt water to the *palha* wax while melting it. *Arenosa* is a more friable, porous wax of a pale grayish-green color produced at the will of the native worker.

FIGURE 6. A primitive press for extracting carnauba wax. The wax when melted is strained through a cloth and the residue squeezed out under a heated worm-screw block press, and caught in cans underneath.

Instead of filtering the wax as above described, the molten wax is sometimes quickly poured through a cheesecloth held by two natives for the filtration, and then the center mass is squeezed with a pair of large wooden pincers to get the wax out of the residue. Some of the modern establishments use a crude type of wooden filter press. The cheesecloth holding the molten wax is placed in a cavity in a log over the bottom of which strong fibers have been stretched. A block is placed on top of the folded cheesecloth, and a long heavy pole is used as a lever to express the wax from the cake. The molten wax is caught in an earthenware pan of about 3 kg capacity and allowed to cool; the hardened wax is broken away and hammered into chunks, and the residue is recovered later.

Theyield of wax per leaf varies with the age of the tree, the locality, and the amount of rainfall which preceded the harvest. On an average a leaf will yield about five grams of wax. With a maximum cutting of twenty leaves per year from a tree, five carnauba palms will produce above one pound of wax a year. The measure for carnauba wax is the *arroba*, equivalent to 33 lbs. About 15,000 to 30,000 *palhas*, or 28,000 *olhos* are required to make one *arroba*. The average yield of the wax for each tree is only 2.8 oz per cutting. There are probably 50,000,000 trees in production, and of these 20,000,000 are estimated to be in Ceará and Piauhy, and 5,000,000 to 6,000,000 in Rio Grande do Norte.

Grades of Carnauba Wax. Grades of the wax in its preparation have already been referred to. A classification given by the Ministry of Foreign Relations at Rio de Janeiro translates the native names for the various types and denominations into the corresponding English grades:

Portuguese	English
Cera Olho:	
Cera Primiera	Carnauba Wax Yellow #1
Cera Mediana Clara	Carnauba Wax Yellow #2
Cera Mediana Roxa	Carnauba Wax Yellow #3
Cera Palha:	
Cera Gorda	Carnauba Wax North Country #3
Cera Gorda Clara	Carnauba Wax Light Fatty Grey
Cera Arenosa	Carnauba Wax North Country #2
Cera Cauipe	
Tipo Especial, Muito Raro:	Special Type, Very Rare:
Cera Flor	Carnauba Wax Flor

Both the #1 and #2 Yellow are quite alike, the #1 being superior in color only. The "north country" grades, on being melted dry, are referred to as toasted waxes. The refined grade is obtained by careful filtration. The chalky grades come from Rio Grande do Norte, while most of the "north country" grades are furnished by the State of Piauhy; these comprise nearly 55 per cent, the "Yellows" 30 per cent, and the "Chalky Grey" 15 per cent of the production. The latter contains an appreciable amount of moisture (7 to 10 per cent).[132]

Cera Gorda is a type which results from leaves that are over-mature or dried out; hence its gray color. But it is regarded as waxy when contrasted with *Cera Arenosa*, which is chalky. *Gorta preta* is a lower grade which is nearly black in color. In the cleanup of the melting room an accumulation of the unclassified grades produces *cauipe*, which has a dirty-looking color and is sold for domestic use. When the wax melted from the *palha* leaf is cooked, the toasted wax is termed *cera tosada*, and the chalky variety melted with water produces the cooked wax *cera cosida*. These are colloquial terms. Since preference is sometimes given by purchasers for the yellowish grades, carnauba wax is sometimes bleached, and to facilitate bleaching five per cent of paraffin wax is said to be added to the carnauba. But aside from this fact, paraffin is sometimes used as an adulterant.

Properties of Carnauba Wax. The following analytical constants for carnauba wax have been determined by several investigators.

Specific gravity at 15°	1.0008[k], 0.990–0.999[a], 0.995–0.999[b]
25°	0.9988[k]
38°	0.9950[k]
44°	0.9930[k]
90°	0.8484[k], 0.850[a]
94°	0.8455[a]
98°	0.8430[k], 0.8420[a]
100°	0.8415[k]
Melting point	84°[c], 78–85°[d], 83.5°[b], 83.3°[e], 83°[f]
Ubbelohde	83°[f]
Ring and Ball	85°[f]
Setting point	82°[f]
Softening point	81.1°[e], 82°[f]
Liquating point	80.6°[f]
Acid value	4.0[g], 4-8[h], 4.2–5.4[b], 5.0[i], 9.7[j]
Saponification value	87–84[a], 79–95[i], 79–82[b]
Iodine number	9-13[a], 7–14[d], 7.2–9.2[b]
Refractive index at 40°	65.7–69.0[a]
Acetyl value	54.8–55.2[a]

[a]Lewkowitsch; [b]Farcy; [c]Wiesner; [d]Sweet; [e]Bulatkin for No. 1 carnauba; [f]Rainer; [g]Hübl; [h]Radcliffe; [i]Allen; [j]Eichhorn; [k]Warth.

Carnauba wax is sparingly soluble in organic solvents at ordinary room temperature, but appreciably soluble in most solvents at a temperature of 45° or more. The following table[147] gives the solubility of carnauba wax in various solvents at a temperature range of 25 to 30°.

Solvent	Solubility	
	gm per 100 ml solvent	gm per 100 gm solvent
Ethyl ether	0.421	0.594
Methanol	0.179	0.226
Ethanol (95%)	0.141	0.174
Benzene	0.518	0.590
Chloroform	1.690	1.145
Acetone	0.323	0.410
Xylene	0.610	0.709
Ethyl acetate	0.374	0.412
Turpentine, gum	0.440	0.508
Naphtha, high b.p.	0.219	0.281

At 45° 3 grams of carnauba wax dissolve in 100 grams of V.M.& P. naphtha (sp. gr. 0.750 at 15.6°/15.6°; 7 grams in 100 grams of solvenol (terpene hydrocarbons); and 11 grams in 100 grams of turpentine (sp. gr. 0.860).

At 50° 20 grams of carnauba wax dissolve in 100 grams of V.M.& P. naphtha; 11 grams in 100 grams of solvenol; and 21 grams in 100 grams of turpentine.

Chemical Constitution of Carnauba Wax. The presence of a considerable amount of a C_{30} alcohol in both the free and combined state was determined first by Stürcke, who also discovered the presence of a hydrocarbon (m. 59°). Free cerotic acid in carnauba wax was first identified by Bérard. Stürcke prepared the dibasic acid $C_{19}H_{38}(COOH)_2$ (m. 90°) from the lactone in carnauba wax, thus proving the lactone to be an anhydride of ω-hydroxy-1-uncosanic acid (isomer). Leys,[84] at the Municipal Laboratory in Paris, has reported 47.1 per cent of saturated acids (m. 75°) and 49.2 per cent of saturated alcohols. A report of *Rivisto commercitalo-brasil*[7] gives the fatty acids as 47.95 per cent on wax melting at 85°, saponification value 79.8–88.3, and iodine number 13.5. The unsaponifiable was determined to be 54.87 per cent by Allen and Thomson, and the total alcohols as 52.4 per cent by Ashbutt. Lewkowitsch found the acetyl value 55.2 for a sample of wax having a saponification value 79.68.

There is some uncertainty as to whether the wax alcohol $C_{27}H_{55}OH$ (m. 78–79°) exists as such, or as a mixture of C_{26} and C_{28} alcohols, that might show a depressed melting point of 76°. Sweet[132] states that carnauba wax essentially consists of *myricyl cerotate,* and small quantities of free *cerotic acid* and *myricyl alcohol.*

Studies based upon the analyses of Liebermann,[85] of Stürcke, and the most recent, Koonce and Brown,[75] show that carnauba wax comprises the following substances:

(1) A hydrocarbon (m. 59°), probably *heptacosane* ($C_{27}H_{56}$).

(2) An alcohol ($C_{26}H_{52}OH$, m. 76°), probably *ceryl alcohol,* and not necessarily the *n*-alcohol, 1-hexacosanol.

(3) An alcohol ($C_{27}H_{55}OH$, m. 80–82.5°), which has been named *carboceryl alcohol,* an isomer of 1-heptacosanol.

(4) An alcohol ($C_{28}H_{57}OH$, m. 83.2°) identified as *octacosanol* by Koonce and Brown.

(5) An alcohol ($C_{30}H_{61}OH$, m. 86.4–86.8°) which is probably *triacontanol.*

(6) An alcohol ($C_{32}H_{65}OH$, m. 89.4°) in greater proportion than the C_{30} alcohol, and isolated by Koonce and Brown in the proved state of 100 per cent purity, probably *1-dotriacontanol.*

(7) A dihydric alcohol [$C_{25}H_{50}(OH)_2$ m. 103.5–103.8°] convertible to the corresponding dibasic acid (m. 102.5°).

(8) *Carnaubic acid* ($C_{24}H_{48}O_2$, m. 72.5°), described by investigators as an isomer of lignoceric acid (m. 84.2°).

(9) An acid ($C_{27}H_{54}O_2$, m. 82.5°). The normal C_{27} acid, 1-heptacosanic, melts at 87°; hence the acid would need to be an isomer or a eutectic of lower and higher homologs, hexa- and octacosanic acids. The C_{27} acid was that first discovered by Brodie in the

free state, but is now conceded to be a mixed dimer of the C_{26} and C_{28} *n*-aliphatic acids.

(10) Cerotic acid ($C_{26}H_{52}O_2$, m. 79°), which is almost entirely combined with myricyl alcohol to form the alkyl ester *myricyl cerotate.*

(11) An ω-lactone of 21-hydroxy-1-uncosanic acid (m. 103.5°)

In the study made by Koonce and Brown,[75] 400 grams of #3 chalky carnauba wax were dissolved in 500 cc of toluene by heating on a steam bath; 140 grams of KOH were dissolved in 2000 cc of 95 per cent alcohol, and this solution added to the wax. The combined solutions were refluxed on a steam bath for 19 hours. At the end of this period the alcohol and toluene were distilled off, and the residue was heated on the steam bath for 48 hours. The resulting hard cake was powdered in a ball mill, and extracted with ethyl ether in a modified Soxhlet extractor for 475 hours; 216 grams of crude alcohols (54 per cent of the original weight of the wax) were thus obtained. These alcohols had a melting point of 84 to 89°, a saponification value of 0, and a neutral equivalent of 0. Fractional distillation of wax alcohols was conducted on the crude alcohols once crystallized from a 10 per cent solution of toluene. The distillation was carried out in the range of 0.28 to 1 mm pressure. Melting points were determined on eight portions of the distillate, on the third crystallizations of each from acetone. The fractions boiling above 236° were crystalline, and in the form of glistening plates. Acids and ethyl esters of the purified fractional constituents were prepared, and resolidification points, and carbon analyses were run for their identification.

Koonce and Brown also resorted to fractional crystallization of the crude alcohols, and obtained three rather distinct components. One fraction (p-6) was recrystallized from toluene, Skellysolve B, chloroform, and trichloroethylene. The melting points (m.p.), resolidification points (r.p.) and remelting points (r.m.p.) were given for the crystals obtained with each solvent, little difference being observed. The crystalline material melted at 86.4 to 86.8° and resolidified at 85.8°. The acid prepared therefrom melted at 90.8 to 91° and resolidified at 90°. The ethyl ester melted at 71.6 to 72.3°. This corresponds to *myricyl alcohol* or *triacontanol.* Another fraction (p–5_2) melted at 77.3 to 78.1°, resolidified at 77.2°, gave an acid m. 84.5 to 84.8°, which resolidified at 84.2°, and produced an ethyl ester m. 68.3 to 68.6°. This fraction was not over 95 per cent pure.

In the older method of Leys,[84] the saponification was conducted with alcoholic potassium hydroxide and benzene, and the alcohol-hydrocarbon constituents are retained in the benzene. Upon evaporation of the benzene the residue is taken up with hot amyl alcohol and fuming hydrochloric acid to oxidize out the alcohols and leave the hydrocarbons. On this basis the

Municipal Laboratory in Paris reported through Leys that carnauba wax contains the following proportion of its constituents:

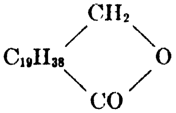
47.1 per cent saturated acids m. 75°, acid no. 78.5.
49.2 per cent saturated alcohols m. 81°.
0 per cent unsaturated acids.
0 per cent hydrocarbons (probably a fraction of 1 per cent).

Approximate Composition of Carnauba Wax

Alkyl Esters of Wax Acids: 80-81 per cent
myricyl carnaubate, m. 78°, m. wt. 789.40
myricyl cerotate, m. 87°, m. wt. 817.46 (75%)
ceryl cerotate, m. 84° (1%)
ceryl octacosanate, m. 86° (1%)
ceryl ω-hydroxyuncosanate, m. 84° (?)

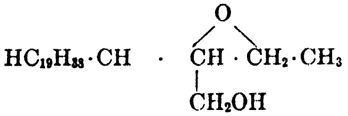
Free Wax Acids: 1-1½ per cent
montanic acid, $C_{29}H_{58}O_2$, m. 83° (C_{28}, C_{30})
melissic acid, $C_{31}H_{62}O_2$, m. 90° (C_{30}, C_{32})
lacceric acid, $C_{32}H_{64}O_2$

Lactones: 3 to 5 per cent
(dimeric) ω-1-lactone of medullic acid, m. 103.5°



Free Monohydric Alcohols: 9 to 10 per cent
carboceryl alcohol, $C_{27}H_{55}OH$, m. 80–82.5° (C_{26},C_{28})
octacosyl alcohol[a], $C_{28}H_{57}OH$, m. 83.2°
myricyl alcohol[a], $C_{30}H_{61}OH$, m. 86.4°–86.8°
lacceryl alcohol[a], $C_{32}H_{61}OH$, m. 89.4° (6%)

Free Polyhydric Alcohols: 1 to 2 per cent
dihydric pentacosanol, $C_{23}H_{46}(CH_2OH)_2$, m. 103.6°
oxy-alcohol derived from the unsaturated alcohol (carnaubanyl alcohol, m. 39°), probable structure,



Hydrocarbons: less than 1 per cent
heptacosane, m. 59.2°

Resins: 3 to 4 per cent

[a] Obtained by Koonce and Brown in the fractional distillation at 0.5 mm pressure of the free wax alcohols directly from the wax, followed by recrystallization of alcohols to obtain them in a state of 95–100 per cent purity. The alcohols (C_{28}), (C_{30}), and (C_{32}) in carnauba wax were definitely established as *n*-aliphatic.

Carnauba Wax as "Melting Point Booster." Carnauba wax is used extensively to elevate the melting point of other waxes, and so is known as a "melting point booster." Lewkowitsch has recorded the melting points of mixtures of stearic acid, ceresin, and paraffin wax, each with carnauba wax, on the basis of values obtained by Valenta.[142] As Valenta's values on paraffin-carnauba melts were determined with a high-melting paraffin [60.5° (140.0° F)], new values were obtained by Bulatkin[147] on paraffin of 54.4° (130.0°F) melting point, since this is the kind most commonly used in America.

Measurements were made in a manner that would accurately determine the shoulder of the curve which lies between the values of 1.25 and 10.0 per cent of carnauba, in the carnauba-paraffin melts.

Carnauba Wax (%)	Paraffin (%)	Melting Point (°C)	Melting Point (°F)
—	100.0	54.4	130.0
1.25	98.75	62.2	144.0
2.5	97.5	76.6–75.8	170.0–168.5
5.0	95.0	79.3	174.7
7.5	92.5	78.5	177.0
10.0	90.0	81.1–78.5	178.0–177.0
20.0	80.0	81.4	178.5
30.0	70.0	81.4	178.5
40.0	60.0	81.7–81.1	179.0–178.0
50.0	50.0	81.4	178.5
60.0	40.0	81.7	179.0
70.0	30.0	81.9	179.5
80.0	20.0	82.2	180.0
90.0	10.0	83.3	182.0
100.0	—	85.5	186.0

The table shows that the main boost in melting point of paraffin may be made with as low as 2.50 per cent of carnauba wax, namely from 130° to 170° F. There is not much occasion to increase the carnauba beyond 3 per cent, which will give a wax blend having a melting point as high as 172.5° F.

In these mixtures the waxes with a high percentage of carnauba wax have a high shrinkage value. Casts made with a high carnauba wax content, that is, over 50 per cent, are quite strong. Those ranging from 40 to 20 per cent of carnauba are weak; the crystallizing forces counteract one another, and this peculiarity is noticed in the melts. There appears to be one mixture of the two waxes, *i.e.*, paraffin and carnauba, in which these forces balance, and that is with about a 15 per cent of carnauba. Below 10 per cent of carnauba the wax compositions are strong.

Under water the softening points of carnauba-paraffin blends are considerably below their respective dry melting points, and this factor proves highly disadvantageous when the blended wax is to be used to coat paper containers that come into contact with hot liquids. Carnauba and paraffin form a mixture which is not a true solution, and it is generally believed that the resinous constituent of the carnauba more or less covers the particles of the lower-melting paraffin, thus boosting the dry melting point.

Separation of carnauba constituents from the paraffin mixture is frequently noted in handling the blended wax.

Refined Carnauba Wax. A so-called refined carnauba wax has been prepared in Germany and Austria by first mixing paraffin with the natural wax, then saponifying with alkali, next boiling the saponified mixture with water, and finally separating the waxy layer containing paraffin, etc., from the aqueous soapy solution; after this treatment, the wax may be readily bleached. By acidifying the soapy solution "carnauba wax residues" are obtained. These residues give the following average constants: m.p. 67–68°; acid value 21.6–22.2; ester value 10.6–12.2; saponification value 32.2–34.4. The refining method permits the utilization of the cheap lower grades of natural wax. The refined carnauba wax is white in color, is non-saponifiable, and has a very low viscosity when melted.

FIGURE 7. The large wax consumers have their own store rooms where they keep a good reserve of the carnauba wax packed in jute bags.

Uses of Carnauba Wax. *Carnauba wax* has been called the mainspring of the floor-polish industry, and no entirely satisfactory substitute has been found for it. The value of the carnauba constituent in such polishes lies in the fact that it produces the most durable luster and hardness. *Candelilla* and *ouricuri wax* have been used to some extent as substitutes, but are inferior. *I.G. Wax OP*, a synthetic ester wax of very high melting point has been used in floor polishes. This OP wax, however, must be used in conjunction with carnauba. The OP wax has very great oil-absorption power which is an important requirement in the paste polishes. *Petrolatum wax* of the harder grade is sometimes used with carnauba to prevent slipping on a highly polished floor. Its use is limited to 10 per cent or less of the total waxes in the water-emulsion type of polish.

Carnauba with montan wax is used for the recording records on phonographs, as the mixture will take a very fine tonal impression, which can then be transferred to copper by plating to produce the master record.

Carnauba wax is used in leather dressings. It plays an important part in the manufacture of carbon papers, and as a hardening agent for candles. A considerable amount of carnauba wax is used for the manufacture of cheap artificial ceresins, which usually employ about 5 per cent. Carnauba has certain disadvantages for electrical use because of the great shrinkage that it undergoes in passing from the liquid to the solid state. The uses of carnauba in various formulas are described elsewhere in this book. Shoe creams with a characteristic "ring formation" on the surface due to the *myricyl alcohol* of the carnauba wax are much sought after in the trade.

Carnauba wax enters into the manufacture of photographic films, chalk, matches, soap, unguents, dry batteries, citrus fruit wax dips, etc., the carnauba generally being used in conjunction with other waxes.

Carnauba wax is used for staining interior woodwork. One pound of carnauba wax is dissolved in a gallon of toluene and a colored dye is added in an amount sufficient to give the desired staining effect.

Sweet[132] lists the consumption of carnauba wax in the various industries as follows:

	Consumption (pounds)	Amount (pounds)	Grade Used
No Rub wax emulsion—floor polish	5,760,000	2,680,000	No. 3
		1,580,000	No. 2
		1,500,000	No. 1
Leather dressing and shoe polish	4,480,000	3,000,000	No. 3
		480,000	No. 2
		1,000,000	No. 1
Paste and liquid polish for floor and auto	2,240,000	1,680,000	No. 3
		560,000	No. 2
		1,000,000	No. 1
Carbon paper and coating	1,920,000	1,000,000	No. 3
		920,000	No. 2
Paper sizing and polish	480,000	480,000	No. 1
Paper impregnating, bottle caps, etc.	320,000	320,000	No. 3
Miscellaneous	800,000	500,000	No. 1
		300,000	No. 2

The principal grades offered in the New York market and their prices for December 1941 were as follows:

Grade	Cents Per Lb
#1 Yellow	82
#2 Yellow	89
N.C. #3	74
Chalky	70
Refined #3	81½

The greater demand on the Brazilian shippers was for the North Country #3, and the Refined #3. Parnahyba is the chief port of shipment for carnauba wax.

The total exports of carnauba wax in 1939 were approximately 11,000 short tons, of which the United States took about 75 per cent. The imports into the United States were about 9,000 short tons in 1943, and were expected to increase greatly in 1944.

Palm Wax

Palm wax is a resinous type of wax derived from the lofty wax palm, *Ceroxylon andicolum*, Humb., indigenous to the South American Andes. A naturalist states: "Try to imagine a palm having a cylindrical, smooth, shining, alabaster-like trunk which rises, shaft-like, 200 feet and more straight into the air and bears at its summit a crown of feathery, silvery green leaves, nearly 20 feet in length. Then visualize it standing either solitary or in company with others of its kind at nearly 10,000 feet above sea level, within sight of perpetual snow." This is the tallest of all wax palms; it is the wax palm of the Quindio Pass in Colombia.

The various kinds of wax palms, at present united under the genus Ceroxylon, are now to be seen widely distributed along the length of the Andes, occurring mainly at remarkably high altitudes from Venezuela and Colombia into southern Peru. The general altitudinal limit of the palm family as a whole is somewhat less than 4000 feet. There is a species of wax palm growing at the boundary line between Colombia and Ecuador which averages 40 to 50 feet in height, at an altitude of 13,450 feet above sea level.

It was in 1801 that Alexander Van Humboldt, the renowned naturalist, discovered the first species of wax palm. He named it *Ceroxylon andicolum*, the wax palm of the Andes. It was already known locally as the *palma de cera*. The genus name, Ceroxylon, comes from the two Greek words, *keros* (beeswax) and *xylon* (wood); the specific term, *andicolum*, means "of or belonging to the woods." He described the trunk as coated with a shining white wax, which makes it look like an alabaster column.

The wax is usually scraped from the trees, but sometimes the palms are felled first. Upon the trunk of the tree, in the rings left by the fall of the leaves, the wax is about one-sixth of an inch thick. It is in the form of a greenish-white powder, and is gathered and melted down over a fire. The natives use the wax to make tapers, since it burns with a clear, bright flame.

Thorpe[134] states that the wax is obtained by felling the tree and scraping off the coating, which is then boiled with water. Thus softened the wax floats to the surface and impurities are removed. One tree is said to yield 25 pounds of wax. It is made into little balls and dried in the sun. That obtained from the Indians is yellowish-white, porous and friable. When melted it is dark yellow, slightly translucent, and fragile like resin. It is partly wax and partly resin, and it is said to become strongly electrostatic by friction. If the mixture is dissolved in hot alcohol and the wax fractionally separated or freed from resin, the purified wax has a much lower melting point and resembles beeswax. Palm wax, according to Vauquelon, contains two-thirds of a resinous substance and one-third of pure wax constituents. It is reported that the wax constituents differ little from those of carnauba.

Commercial Palm Waxes. The palm waxes of commerce differ somewhat from the above description. The commercial palm wax, when free from paraffin, is a very hard, resinous wax of olive brown color, and well may be licuri wax (*Cocos coronata*). It has a durometer hardness of 100 at 15°, and 97 at 25°. It begins to sinter and soften at 74 to 75° in a capillary tube, and melts at about 85 to 86° to a viscous liquid. It has a density of 1.0464 at 9°, 1.0447 at 16°. Its coefficient of cubical expansion is 0.00023. The wax has an acid value of 10.6, and iodine number of 16.9 (Hanus), and a saponification value of 103.9. It is said that the wax cannot be refined by chemical bleaching or otherwise without the addition of paraffin.

Palm waxes in the New York market are not in any sense genuinely derived from the sources described. They are generally considered as "replacement waxes" to be used in the arts in place of the more expensive carnauba wax. They are prepared by blending some of the harder vegetable waxes with paraffin, and unfortunately not in standardized amount, but in accordance with a predetermined cost. Generally speaking, the lighter the color the greater the content of paraffin. The following analyses were made of commercial specimens.

Color	M. P.	Density at 15°	Hardness (Durometer)	Acid Value	Sapn. Value	Iodine No.	% Paraffin Indicated
Pale brown	82.2°	0.9950	92	3.84	29.0	2.54	30
Yellow	80.0°	0.9510	77	4.42	31.0	2.76	57
White	71.1°	0.9000	60	—	—	—	88

Since the melting point of commercial palm wax is high, the addition of this wax to paraffin will elevate the melting point of the paraffin. For example, when 2 per cent of palm wax are added to paraffin of 131° F melting point, the blend will have a melting point of 138° F (58.9°). When 5 per cent are added, the melting point is elevated to 147° F (64°). Palm waxes have a pleasing odor, somewhat different from carnauba, and are of sweetish taste. Added to ceresin, commercial palm wax will prevent oxidation of the hydrocarbons when the ceresin is subjected to continuous heating. White commercial palm wax is the equivalent of a cheap artificial ceresin.

Ouricuri Wax

Ouricuri wax, also known as uricuri, uricury, oricury, and ouricoury, is a wax derived, according to Ivanovszky,[67] from the under surface of the leaves of a tall palm, *Attalea excelsa*, Martin. It is sometimes called the cohune palm, and grows in tropical America. A closely related species, *A. funifera*, Mart., the bast palm, furnishes fiber known as piassava for cordage. The palm furnishing *ouricuri wax* has also been referred to as the uricury wax palm and classified by Kew Royal Botanical Gardens as *Syagrus coronata*, Becc. Rowan refers to the wax as *ouricuri wax*, and as derived from *Cocos coronata*, Martin, a species of coco palm, growing in north and east Brazil; however, this species, according to Silva, Rio de Janeiro, produces "Ouropaido wax," (licuri wax) which is not the same but appears to be closely related to ouricuri.

Ouricuri wax is scraped off the leaves with a knife and is collected in the form of a powder. This powder, representing 0.48 per cent of the dry leaves, is passed through mechanically moved sieves. After being melted in a rotating melting pot heated by circulating hot water, the wax is run off into forms, cooled, and solidified into small blocks. These blocks are then sacked for export.

The grade which has been known since 1938 as machine-processed ouricuri wax is very hard (durometer test 100 at 25° or below) and in color is not unlike the darker grades of carnauba. In general, ouricuri is a dense, hard, brittle, yellow wax.

It has been reported that a refined quality of ouricuri wax, known as Brazilian double-refined wax, is prepared by digesting the scrapings of the palm in a caustic soda solution with the aid of steam, the vegetable matter sinking to the bottom of the tank and the wax, freed from an appreciable amount of plant resinous material, rising to the top in the operation as the water is boiled off. The high gravity of the wax does not permit its separation from the plant material in the usual way in which waxes are separated.

The refined wax as above prepared comes into the market in the shape of blocks, and is recognized by its low saponification value.

Properties of Ouricuri Waxes. The physical and chemical constants of the ouricuri waxes are tabulated below.

	Ouricuri Natural (A. excelsa)	Double Refined (Brazilian)	Licuri Natural (C. coronata)[91]	Licuri Refined (Brazil)
Sp. gr. 15°/4°	1.0685	1.0561	1.0100	0.9980
Sp. gr. 25°/4°	1.0661	1.0535	——	——
Melting point (°C)	84.3	79.0	84.5	83.8
Solidifying point (°C)	72.2	68.9	——	——
Acid value	23.8	21.1	12.0	3.0
Saponification value	85.3	61.8	109.2	85.8
Ester value	61.5	40.7	97.2	82.4
Iodine number (Hanus)	7.1	6.9	15.2	7.8
Ash (%)	1.91	0.55	——	——

A fatty grade of machined processed ouricuri wax had a melting point of 87°, acid value 71, saponification value 110, iodine number 17.2, and durometer hardness 100. American refined ouricuri is the designation given to the crude wax which has been remelted and filtered to remove mineral or other foreign matter, and is produced and marketed in both lumps and flakes. The flakes have a melting point of 83.3°, the melt solidifying at 72.9°. The great spread between the melting and solidifying points is characteristic of the ouricuri waxes, a property which is not found in carnauba wax. The saponification value of a sample of flakes is about 108.

Ouricuri wax, crude, has a cubical coefficient of expansion of 0.000244 at 25°, and 0.000604 for the melt.[149] The refined wax has a coefficient of cubical expansion of 0.000361 at 25° and 0.000668 for the melt. The shrinkage of ouricuri wax in its transition from the molten to the solid state (25°) appears to be greater than that of other known waxes. The coefficient of cubical expansion of the solid crude wax, namely, 0.000244, is also lower than that of any other.

Ouricuri wax is sparingly soluble in the polar solvents, such as alcohol and acetone, and only partly soluble in the non-polar solvents, such as benzene, carbon tetrachloride and chloroform, in the cold. The wax is soluble in 95 per cent ethanol at 25° to the extent of 0.350 gram in 100 ml of solvent, and of 0.350 gram in 100 ml of ethylene dichloride at 37°. In its solubility in solvents it differs little from carnauba wax.

Ouricuri and licuri waxes have a fragrant odor, resembling that of carnauba, but not as fragrant or agreeable. The wax, when powdered, produces a yellow-orange color with 10 to 20 per cent of sodium hydroxide solution; carnauba, on the other hand, produces a colorless solution (motta test).

All the waxes from *Cocos* or allied genera of palms are believed to contain substantially the same constituents in proportions but slightly modified.

They contain *myricyl cerotate,* free *cerotic acid,* or higher homologs, resins, and hydrocarbons, and a very small amount of mineral matter. De Souza Machado[91] reported *cerotic acid* and *melissyl alcohol* in licuri wax (*Cocos coronata*).

The approximate composition of ouricuri wax appears to be about as follows: esters (as myricyl cerotate) 59.0 per cent; free wax acid (as lacceric) 10.4 per cent; neutral saponifiable resins 11.6 per cent; hydrocarbons (as hentriacontane) 17.0 per cent; mineral matter 2.0 per cent.

Uses of Ouricuri Wax. Ouricuri wax is used as a substitute for carnauba wax in floor waxes, shoe creams, and other polishes, although it is somewhat inferior. It is also of value in the inks used in producing typewriter carbon papers as it provides a means of securing sharp definition of type in copy. In paste-type polishes when ouricuri is used to replace carnauba it is generally necessary to modify the recipe. Ouricuri, like carnauba, can be used as a "melting point booster" for paraffin. When 2 per cent of ouricuri wax is added to paraffin wax, the melting point of the latter is raised from 54.4° to 71° (130° F to 160° F), and 5 per cent of ouricuri advances the melting point to 79° (174° F). In this respect there is a close resemblance in its behavior to carnauba wax.

It is reported that ouricuri wax has been used in the finishing of bombing and fighting planes, on account of the high polished surfaces that can be produced with it, so that they are resistant to air friction, and to wetting or condensation.

Starting to appear in export statistics with only 3,075 kg in 1937, ouricuri wax contributed 1,341 metric tons during the first nine months of 1941. In 1942 machine processed ouricuri wax was offered at 32 cents per pound, f.o.b. Bahia, Brazil, and considerable tonnages of this grade have been shipped from Brazil to the United States.

Raffia Wax

The Madagascar sago palm furnishes the fibrous material known as "bass" which is used by gardeners, and which is also of economic value in basketry when properly prepared. The raffia fiber is obtained from the leaf stalks; it is the epidermis of the upper side of the palm leaf. The dull undersurface is coated with a whitish layer or bloom, consisting of wax, which can easily be rubbed off. Raffia wax, also spelled *raphia wax,* is defined as the wax obtained from the dried leaves of the *Raphia ruffia,* Martius. Raphia is a small genus comprising five species of pinnate-leaved palms, family *Sabalaceae,* natives of tropical Africa and South America. The trees have stout trunks, very large spiny leaves, and spicate inflorescences, often six feet in length; they bear a spring fruit which contains a single hard seed. The raphia palm is referred to by Thorpe as

Raphia pedunculata, Beauvois (or *R. ruffia*, Mart.). He gives the following method of extraction for the wax.

After the bass is removed, large quantities of the residues are available as a source of the wax. The leaf residues are spread out to dry on cloths in the open air, but must be sheltered from the wind as the light waxy matter is easily blown away. After drying two to 4 days a white coating is apparent on the under surface of the leaves; this is detached as a powder by shaking or rubbing the leaves between the hands. The powder is collected, freed from foreign matter by sifting, and then put into boiling water; the wax melts and floats on the surface, earthy impurities settling to the bottom. The melted wax is separated and allowed to solidify.

In an experimental trial[134] it was found that ten leaves of medium size (3½ to 4½ meters in length) weighed 104.5 kilograms. From these leaves could be obtained 9.2 kilograms of bass, which produced 4.6 kilograms of clean fiber. The refuse or residues in the green state after removal of the bass amounted to 32.5 kilograms, which when dried weighed 11.0 kilograms, and this yielded 0.81 kilograms of crude, or 0.78 of refined wax. Commercially, the yield of wax is said to be somewhat less than 0.75 per cent of the weight of the leaves.

Raffia wax is a hard brown wax which can be easily pulverized. A lighter colored wax may be obtained by treating it with an oxidizing agent, such as chromic acid, although the bleaching treatment tends to impair the hardening properties of the wax. It has a density of 0.950 at 15°, and a specific gravity of 0.832 to 0.836 when melted (99°/15.5°). Thorpe gives its melting point at 82° to 83°. Haller gives its melting point at 80°; and its boiling point at 280° to 300° (10 mm pressure), with some decomposition.

Thorpe[134] gives the acid value as 4.9 to 6.5, saponification value 51.3 to 50.3, and the iodine value as 7.7 to 10.7. Raffia wax is only slightly soluble in alcohol, ether, acetone, chloroform, light petroleum spirits, and carbon disulfide. It dissolves in boiling benzene, and in boiling alcohol although about 10 per cent separates out on cooling.

Its chemical composition has been reported to be for the most part higher saturated alcohols of the approximate composition, $C_{20}H_{41}OH$, but differing from arachidyl alcohol (m. 66.5°). However, it is more likely that raffia wax contains both hydrocarbons and alcohols of appreciably higher hydrocarbon content, since other leaf blades yield alcohols very high up in the series.

(2) *Waxes from Herbs and Shrubs*

Candelilla Wax

Candelilla wax is obtained from a weed, *Pedilanthus pavonis*, Boissier, or from *P. aphyllius*, which grows in the semi-arid regions of northern Mexico, southern Texas, Arizona, and southern California. Its common names are jumete, and candelilla, and it belongs to the family, *Euphorbaiaceae.* Closely associated botanically are *Euphorbia antisyphilitica,* Zucc., and *E. cerifera*, with the common name "jerba," both of Mexico. The constants of the waxes from these latter species differ somewhat from those of the regular candelilla wax. The Mexican plant is described as occurring in bunches of leafless, reedlike stems 2 to 4 feet high and from ¼ to ½ inch in diameter.[55] The wax forms a coating on the entire surface of the shrub except the root.

Hare and Bjerregaard,[55] of New Mexico, prepared the wax from bundles of plant stems received from Mexico. The bundles were weighed down in cold water to keep them from floating and the water brought to a boil, whence the wax rose to the surface. After cooling the impure cake of wax that floated on the water was removed and dried. It was dark in color. The crude wax was then dissolved in hot chloroform and the solution filtered to free it from fragments of bark and foreign matter.

The chloroform was evaporated off on a steam bath. It was redissolved in a mixture of 3 parts of boiling alcohol and 2 parts of benzene, filtered hot and the solvent evaporated off. In this manner a pale grayish-yellow, opaque solid was obtained. It was remelted and dried to a moisture-free basis. About 2.5 per cent of wax was obtained from the plants. The dried wax is brownish in color, but can be bleached by exposing it to the sun if the wax is first formed in a sheet. Four factories in Monterrey, Mexico extract this type of candelilla wax.

Commercial Candelilla Wax. Dickinson[35] has described the production of candelilla wax at Monterrey, Mexico. After the shrub is pulled out of the earth it is placed in a wooden tank containing water which is then heated to the boiling point. At the moment of boiling, sulfuric acid is put in the tank. As soon as the acid comes in contact with the wax the latter comes to the surface and is collected and withdrawn to a receptacle where it congeals. The crude wax is then transferred to another tank where steam is used to melt it, and sulfuric acid added a second time to refine the wax; the refined wax is withdrawn and allowed to harden in molds. The wax can also be extracted from the shrub by direct fire, by steam, and by benzine. Yields of 3½ to 5 per cent have been reported.

The color-imparting, resinous compounds of crude candelilla wax can be destroyed by the action of chromic acid. If the candelilla is to be used in combination with paraffin, these resinous compounds may be removed by simply melting the wax with three parts of paraffin and either allowing the resinous compounds to settle out or, hastening their separation by filtration with activated chars, fuller's earth or mixtures of these. Good results are also obtainable by treating the candelilla-paraffin mixtures with hydrogen peroxide and potassium permanganate.

Candelilla wax in commerce is marketed in opaque lumps that are brownish or yellowish-brown in color, hard, brittle and easily pulverized. Its surface is capable of taking a high polish, and it is this property which imparts a luster to polishes. Candelilla wax has the odor of beeswax when warmed, and burns with a bright flame. It is only soluble in cold ether to the extent of 0.12 gram in 100 cc, and even less soluble in ethanol. It is sparingly soluble in cold chloroform, turpentine, gasoline, carbon bisulfide, or acetone. It is readily soluble in all of these solvents hot. About 4 to 5 grams of candelilla wax dissolve in 100 grams of turpentine or turpentine substitutes at 25°, and the same amount in pine oil at 35°. A mixture of 3 parts of absolute alcohol and 2 parts of benzene (90 per cent) makes an excellent hot solvent.

Properties of Candelilla Wax. The physical and chemical constants of candelilla wax as derived from various sources have been determined by Hare,[56] Lüdecke,[60] Sanders,[120] and Deiler.[45] Farcy[41] has published constants on the Mexican variety, *P. aphyllius*, which apparently contains fewer hydrocarbons, namely 33 per cent contrasted with 50 to 53 per cent for *P. pavonis*.

At the Tezonapa Botanical Station, Olsson-Seffer and Sanders[108] examined the wax of *E. antisyphilitica*, which apparently differs a little from that of *P. pavonis*, and found it less resinous, and lower in both acid and iodine values. The wax also had a higher melting point.

Constants Reported for Candelilla Wax (*Pedilanthus spp.*)

	Hare	Lüdecke	Sanders	Deiler	Farcy	Leys
Acid value	12.4	8.9–19.0	14.4	19.0	20.0–21.0	19.4
Sapn. value	64.9	54.0–61.4	46.7	59.7	66.0–67.0	53.5
Iodine number	36.8	13.0–22.9	16.6	14.0	20.0–21.0	12.9
Density at 15°	0.9825	0.9416–0.9960	0.9850	—	1.001–1.002	0.9910
Melting point	67–68°	68.7°	67.5°	66.0°	64–65°	71°

Constants Reported for Candelilla Wax (*E. antisyphilitica*)

	Olsson-Seffer	Sanders
Acid value	0.32	0.03
Sapn. value	104–108	105–106
Iodine number	5.23	5–6
Density at 15°	0.9473	0.9587
Melting point	77.4°	74–80°

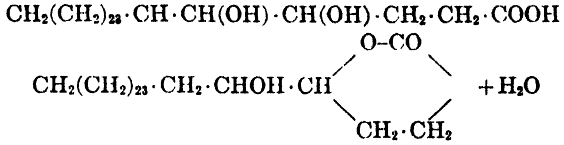
Mean Values for Candelilla Wax of Various Species

	P. pavonis	*E. antisyphilitica*	*E. cerifera*
Acid value	16.6	0.2	15.4
Sapn. value	58.1	105.7	60.7
Iodine number	19.8	5.4	17.4
Density at 15°	0.9857	0.9530	0.9838
Melting point	67.5°	77.2°	68.0°

As generally described candelilla wax melts at 66 to 68°, and solidifies at 64.5°. The specific gravity is 0.9825 at 15°/15° (Hare) and 0.8700 at 100/15° (Deiler). Buchner determined the acid value as 16.9; Hare and Bjerregaard[55] as 17.4 (on an ash-free sample); and Deiler as 19.0. Buchner determined the ester value as 33.8; the mean value of other investigators is 41.4. Hare determined the saponification value of a rendered ash-free sample as 84.1, and 64.9 in its original state; but the mean value of others is 57.6. Berg found 67.5 per cent unsaponifiable matter in candelilla wax; Hare 84.2 per cent on his ash-free sample. The refractive index of candelilla wax in its original state is recorded as 1.4555 at 71.5°. Determinations made by Olsson-Seffer were on the wax extracted from the plant by means of boiling water, but not subjected to further refinement.

Chemical Composition. Sanders[120] determined the constants on a sample of candelilla, which had been prepared from plants collected in the month of January in Coahuilla, Mexico. The wax was of a greenish-white appearance and had a granular fracture. The dry wax contained 77.0 per cent of unsaponifiable and 48.6 per cent of hydrocarbons. *Hentriacontane* and *myricyl alcohol* were identified as constituents. Hare[55] found that candelilla wax on combustion yielded 80.3 per cent hydrocarbons and 12.7 per cent hydrogen. Deiler's work on candelilla has been described by Fraps and Rather[45] of the Texas Agricultural Experimental Station where the work had been conducted.

The chemical composition of candelilla wax has been studied by Meyer and Soyka[103] who extracted the wax with 96 per cent ethanol to remove traces of resin. By distillation with zinc there resulted a colorless oil, b. 223 to 245°, which had the properties of a sesquiterpene. The resin-free wax was then extracted with hot ethanol which removed 74–76 per cent of what they believed to be *dotriacontane*, m. 71°, b. 310°. The residue (5–6 per cent), m. 88°, they considered to be a *hydroxy lactone*, $C_{30}H_{58}O_3$, which reacts neutral, is stable to $KMnO_4$ in alcoholic solution, and bears a similarity to an OH-lactone found in wool fat. The lactone is possibly δ *hydroxy-*γ myricino-lactone derived from a dihydroxy derivative of an unsaturated acid:



The lactone has an m.wt. of 466.78 and an ester number of 120.

Fraps and Rather (1910) had powdered and saponified the wax with potassium alcoholate, evaporated off the alcohol, and then extracted the dried residue with ether for 40 hours. The yield was 40 per cent, and the extract when recrystallized from ether gave a batch of crystals, m. 68°, identified as *hentriacontane*. The latter substance consisted of white crystals, readily soluble in hot ether, and fairly soluble in cold, insoluble in cold ethanol, but slightly soluble in hot. The hydrocarbon contained 85.48 to 85.16 per cent carbon and 14.10 to 14.28 per cent hydrogen. A resinous solid accompanying the hydrocarbon in small amount was found to be brittle when dry, and of 55° melting point.

Berg[13] in 1914 reported candelilla wax to contain two hydrocarbons to the extent of 50 per cent, two sterols to the extent of 10 per cent, a small amount of ester, and a small amount of what appeared to be a lactone. Hare emphasized the presence of a higher alcohol as a major constituent together with an ester, and some free fatty acid. Farcy[41] in 1920 reported 33 per cent of hydrocarbons. A closely associated wax derived from *E. cerifera*, Alcocer, was reported by Alcocer and Sanders[1] to contain hydrocarbons between C_{31} and C_{35}, the mixture melting at 67–68°.

The approximate composition of the wax from *P. pavonis* on the basis of 67.5 per cent of unsaponifiable appears to be about as follows:

Esters with Hydroxylated Acids: 33-35 per cent
  sitosterol, $C_{29}H_{49}(OH)$ combined with dihydroxymyricinoleic acid, $C_{30}H_{62}O_4$, ester value 195, m. 88–90° (Berg) 20%
  myricyl dihydroxymyricinoleate

Lactone: 5-6 per cent
  hydroxy myricino lactone, m. 88° (M. & S.)
    (from dihydroxymyricinoleic acid)

Free Acids: 9-10 per cent
  cyclic: resin acids
  aliphatic: dihydroxymyricinoleic acid, m. 69° ? (4.2%)

Hydrocarbons: 50-53 per cent
  hentriacontane, m. 68° (40%)
  tritriacontane, $C_{33}H_{68}$, m. 71–72°

Moisture and Volatile Matter: 1 per cent

Density and Coefficient of Expansion. The density of a specimen of candelilla wax as received from the refinery was 0.9956 at 15°, but by remelting and resolidifying the density was lowered to 0.9846.[149] This pronounced difference has also been observed by the author for certain specimens of carnauba wax believed to be "solvent extracted," but not on those that are dry refined. Resolidification was conducted by slow cooling, although rapid cooling made no pronounced difference in the density.

Densities of Commercial Candelilla Wax (m.p. 70.5°)

In lumps from refinery	After remelting and casting in tin
27.8°/15° 0.9911	26.7°/15° 0.9803
44.4°/15° 0.9823	39.7°/15° 0.9752
	47.2°/15° 0.7723

	Density at 25°/15°	at 35°/15°	at 77°/15°	at 100°/15°
Original (as received)	0.9919	0.9874	0.8670	0.8550
Remelt (slowly congealed)	0.9809	0.9770	——	———

NOTE: Densities at 25° and 35° are computed, those at 77° and 100° on molten wax were determined by means of a Westphal balance.

The density increments at 25° are 0.00047 and 0.00039 for the "original" and "resolidified" waxes. Above 50° candelilla wax expands rapidly with increasing applied heat until it begins to flow. In the molten state the expansion is less rapid, as the density decreases 0.00051 per temperature degree. This behavior is not uncommon to that of waxes in general, but is particularly like that of the harder waxes such as carnauba and ouricuri.

The volume decrease of candelilla wax during solidification and crystallization is 12.4 per cent for the "original," and 11.5 per cent for the same wax "remelted and recast." Candelilla wax has a mean cubical expansion coefficient of 0.000404 at 25°, and 0.000608 at 100°. The only waxes with a lower coefficient are carnauba and ouricuri, all determinations being made on specimens remelted and solidified in the air with slow cooling.

Wax Blend of Candelilla and Paraffin Wax. The dry melting points here given for various blends that have been made with candelilla and paraffin wax (128°/130° F m.p.).

Per Cent Candelilla	Melting Point °C	°F
0	54.0	129.2
5	55.0	131.0
10	58.0	136.4
20	60.4	140.8
30	61.2*	142.3*
40	61.5	142.7
50	62.6*	144.7*
60	63.4	146.1
70	63.7*	146.8*
80	64.6	148.3
90	66.6*	152.0*
100	70.5	159.0

* Computed from plotted curve.

It will be noted that the addition of 20 per cent of candelilla wax to paraffin appreciably increases the melting point of paraffin, but with 20 to 80 per cent candelilla there is little further increase. There is, however, a pronounced rise in the melting point of the blended wax as the candelilla content exceeds 80 per cent.

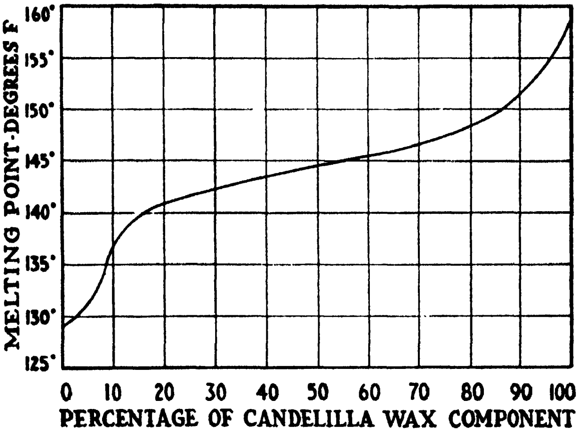


FIGURE 8. Graph showing increase in melting point of paraffin by addition of candelilla wax.

The addition of candelilla to paraffin wax increases the hardness of the latter as is shown in the table of durometer hardness for the candelilla-paraffin wax blends. The paraffin wax component had a melting point of 54°.

Per Cent Candelilla	Durometer Hardness (Shore units at 86°)
0	70
5	70
10	80
20	84
40	94
60	98
80	100
100	100

It will be observed that the addition of more than 5 per cent of candelilla wax tends to greatly harden the paraffin, and that with 80 per cent candelilla the wax is stone hard.

Uses of Candelilla Wax. Candelilla wax is used quite extensively to harden other waxes. Its melting point is lower than that of carnauba wax, and it is therefore infrequently used as a melting point extender for wax compositions. It is commonly found as an ingredient in shoe polishes, floor pastes, phonograph records, sealing wax, candles, electrical insulators, waterproof boxes and fabrics.

As a finishing material in the textile industry Herbig[60] states that candelilla wax can be used in the following recipes of emulsions with effective results.

	I	II
Pale candelilla	2.5 kilograms	4.0 kilograms
Japan wax	2.5 kilograms	—
Rosin	—	1.0 kilograms
Potassium hydroxide	0.5 gram	0.5 gram
Sodium hydroxide	50.0 grams	50.0 grams
Water	30.0 liters	28.0 liters

Alcocer Wax

The plant stems of *E. cerifera*, Alcocer, yield a wax which is apparently almost identical to candelilla. Alcocer and Sanders[1] reported that the Mexican plant yielded 2½ to 5 per cent of wax on the dry plant basis, and that the physical and chemical constants of the wax vary with the age of the plant and the year in which it is collected. Plants grown on the coast contain less wax and more caoutchouc latex than those grown in the interior. The constants are recorded as follows: density 15° 0.9820–0.9856; refractive index *n* 85 1.4545–1.4626; acid value 12.73–18.11; saponification value 35.0–86.5; R-M number 0.53–7.69; iodine number 14.42–20.40; non-saponifiable 76.70 to 77.27 per cent; hydrocarbons 42.49–59.70 per cent. The wax is soluble in chloroform, warm ether, benzene, and turpentine. The wax is believed to be of about the same chemical composition as the regular candelilla wax, but may contain amyrin triterpenoids.

Alcocer wax is recommended for the same uses as the regular candelilla of commerce.

Madagascar Waxes

Vegetable waxes are produced in Madagascar from plants botanically classified by Herbert and Heim[59] as *Cyanchum messeri*, *Euphorbia xylphylloides*, and *E. stenoclada*. The dried cut pieces of the plant stems are pounded on a cloth and then thrown into boiling water; the wax is skimmed off as it floats to the surface. The first species of plant yields the most wax—about 7 ounces from six small plants. The interesting feature of these waxes is their hardness, luster and very high melting point. The Madagascar waxes contain little free acid, and are believed to be composed of esters of *sitosterol* with hydroxylated acids, an appreciable amount of *ceryl* and *melissyl alcohols*, the hydrocarbon, *hentriacontane*, and possibly higher homologs. The constants for the waxes are as follows:

	C. messeri	*E. xylphylloides*	*E. stenoclada*
Melting point	88.0°	88.0°	88.0°
Acid value	17.7	28.0	19.3
Sap. value	159.6	142.8	140.0
Iodine number	3.2	5.3	5.9
Hydrocarbons	11.0%	14.0%	15.0%

One of the above waxes, *E. stenoclada*, Baill., is obtained from a tree commonly known as the "Rhimba tree." Madagascar rhimba wax has been briefly referred to by Lewkowitsch.[83] It appeared in commerce some years ago in the shape of small irregular masses adhering to pieces of bark from the tree. Lewkowitsch regarded the commercial wax as a mixture of vegetable wax and resin. Botanically the plants are related to those which produce candelilla wax. The melting points of the Madagascar waxes are higher than those of any of the natural waxes.

A wax from the palm, *Raffia ruffia* is also obtained in Madagascar (see raffia wax, p. 112).

Snow Brush Wax

A Wax may be obtained in large yield from the surface of the plant *Ceanothus velutinus*, Douglas. The shrub is rich in tannin and wax, and is a fire menace in the California forests. The snow brush is a widely branching shrub two to six feet in height, and its habitat is bounded by the Coast Range of California on the west, the Columbia River on the north, Colorado on the east, and San Francisco on the south. It is plentiful in the Shasta National Forest in the neighborhood of Sisson, California.

The brush can be ground, sifted, and extracted with gasoline or other suitable solvent, and the leaves will yield 7.3 per cent of wax, according to Scalione and Blakemore.[121a] The wax has a greenish appearance, is somewhat brittle, and breaks with a conchoidal fracture. The constants on a specimen were as follows: melting point 78–79°; specific gravity 15° 0.988; acid value 20.3; saponification value 93.4; iodine number 19.3; and Reichert-Meissl number 7.5.

The high R-M number indicates the presence of an appreciable amount of soluble fatty acids over and above that associated with glycerides. The commonest of the R-M acids in plants is isovaleric, which is customarily found in the combined state as an ester with a sterol or a terpeneol, the latter being fairly common to plants of a type similar to Ceanothus. The wax of *C. velutinus* is known to contain ceryl alcohol, palmitic and stearic acids, hydrocarbons and resins, and assuming that it is also made up of α- or β-amyrin isovalerate, its approximate chemical composition would be:

Alkyl Esters of Fatty Acids: 80–81 per cent
- ceryl palmitate
- ceryl stearate

Triterpenoids: 5–6 per cent
- α- or β-amyrin isovalerate

Free Acids: 9–10 per cent
- resin
- melissic acid (2%)

Hydrocarbons: 3–4 per cent

It has been estimated that 100,000 tons of the shrubs are available in the Sisson district alone, and if worked, 5000 tons of this wax might be marketed. The nature of the wax is such as would indicate that it might have important uses. Along with the wax it would be possible to recover tannic acid, which constitutes seven per cent of the weight of the plant, and which can be used for tanning hides.

Flax Wax

The outer epidermal layer of the flax stem, *Linum usitatissimum* L., is rich in a wax which remains on the fiber through the retting and scutching operations, in the preparation of the bast fibers for the making of linen. The waxy matter is largely removed in the combing and drawing processes and is found in the dust (pouce) to the extent of about 6 per cent, from which it is obtainable in commercial quantities. Brown linen yarn will yield the waxy material in small quantities by solvent extraction, and the extractive a considerable amount of saponifiable. The bleaching of linen yarn removes the waxes, as the treatment involves the use of soda ash and lime.

Flax and its waste products, according to Chilikin,[28] contain up to 2.5 per cent of wax-like substances, extractable by benzene; these substances increase to 8.7–13.7 per cent in flax dust. Gibson[50] states that the extraction of compressed blocks of the dust leaves a material usable in the manufacture of insulating board. A plant might be profitably operated if it were set up to extract the wax from 100 tons of dust yearly, but it would be more satisfactory for mills to supply dust to a central plant capable of extracting 1000 tons a year.

Higgins[61] studied the behavior of the waxes in the bleaching of textile fibers. He extracted brown linen yarn with various solvents applied in the order of the results given below: ether 1.39, benzene 0.29, ethanol 0.49, hot water 2.03, boiling ammonia 3.27, boiling caustic under pressure 14.06, and hydrochloric acid 0.33. The waxy material removed by the first three solvents contained 27.8 per cent saponifiable matter; but if the extraction was preceded by lime boiling and souring 40.0 per cent of saponifiable matter was obtained. Water-retted flax yields 0.7 per cent more wax than dew-retted. Ether extractions increase the tensile strength of the yarn. Lime boiled and soured, as well as acid treated, linen yields more wax to ether or benzene than untreated linen.

The composition and properties of the wax do not vary much with the source and manner of retting the flax. Among commercial waxes it most resembles beeswax, though it is more brittle and hard. In color, flax wax is dark green or brown; the green of the chlorophyll becomes brown through retting. Hilditch[62] gives the following chemical and physical constants for flax wax (ostensibly the dark green or semi-crude): specific gravity 15°/15° 0.908, m.p. 61°–70°, saponification value 100–150, saponification equivalent 375–360, iodine absorption number 9–17, free fatty acids, acid value 24–26 as oleic acid 12–28 per cent.

The air dried cortical tissue separated from the flax fiber contains about 10 per cent of flax wax, the spun fiber 1 to 2 per cent removable by organic solvents. The wax has a saponification value of 77.5–83.7, iodine number 21.6–28.8, acid value 17.5–23.8, sp. gr. 0.963–0.985, m.p. 67.3°–69.8°.

Irish flax is reported to yield a wax having 70 per cent of unsaponifiable and wax alcohols, 28.2 per cent fatty and wax acids, Reichert-Meissl number 3.2, and ash 0.62 per cent. The wax after being subjected to superheated steam distillation has a saponification value of 70.2, acid value 33.0, and iodine number 18.0.

Hoffmeister[63] reported that the wax or flax extracted by ether or benzine from flax threads and deposited from these solvents in grains of an indistinct crystalline structure had a melting point of 61.5°, and a sp. gr. 0.9083 at 15°. He stated that the wax can easily be obtained from "flax dust" of the spinning-house, of which it forms about 10 per cent. He gave the following constants: acid value 54.49, saponification value 101.51; ester value 49.54, R-M number 9.27, iodine number 9.61 and Hehner number 98.31.

Hoffmeister had separated flax wax into a hydrolyzable and a nonhydrolyzable portion, and in the latter found what he described as a paraffin-like ceresin, m.p. 68°, sp. gr. 0.9941 at 10° (probably *hentriacontane*). An appreciable amount of *palmitic acid* was found but very little *stearic acid.* The acetyl derivatives revealed the presence of *phytosterol,* and *ceryl alcohol.*

The chemical composition of flax wax has been given by Chiliken and Kamolova,[28] who state that it contains *neoceryl alcohol, ceryl alcohol, myricyl alcohol,* a hydrocarbon, m. 62°, corresponding to *nonacosane, cerotic acid, stearic acid, palmitic acid* and *linoleic acid.*

Flax wax will take on a high polish, and thus makes a suitable polishing ingredient for shoe polishes and creams. Flax wax might be used to advantage as a substitute for beeswax in some recipes. Flax wax can be chlorinated to 36 per cent chlorine but the chlorinated wax is not stable at boiling temperature. Cotton fabric treated with chlorinated wax was weakened because of the liberation of traces of hydrochloric acid.

Cotton Wax

Raw cotton fiber, *Gossypium spp.,* contains about four per cent of oil, wax, and resin. Because of these waxy and oily substances raw cotton and unbleached cotton yarns and cloth are difficult to wet through with water. The wax was first isolated in a pure state by Edward Schunck, of Manchester, who in 1868 was investigating the nature of the substances other than cellulose contained in cotton. Schunck reported the wax to have a melting point of 85.5° (186° F); he also obtained from the wax a white solid fatty acid melting at 55.5° (132° F). Schunck found, besides the wax, two distinct coloring matters, one of which was alcohol-soluble: pectic acid and albuminous substances. The yield of wax extracted by Schunck from cotton fiber was only 0.004 per cent.

In subsequent years benzene extractions of cotton fibers were reported with yields of 0.09 to 0.53 of the waxy constituents. More recently Conrad reported 0.4 to 0.7 per cent of wax for most cotton lints, and much higher yields for certain green cotton lints (see green cotton lint wax, p. 127).

According to Knecht and Allan,[70] a petroleum ether extraction of the cotton yielded an odorless, dull yellow substance, closely resembling beeswax in texture and fracture. By repeatedly treating this substance with boiling ethanol, 18.80 per cent of an insoluble glassy wax with a melting point of 78°, and an iodine number of 11.3 remained. The Knecht-Allan separation of the components of the glassy wax will be referred to later.

The analytical constants for crude cotton wax are as follows: sp. gr. at 15°, 0.965–0.980; m.p. 64–66°; acid value 38–45; saponification value 159–178; unsaponifiable matter 28–34 per cent.

Tonn and Schoch[134a] have investigated a semi-refined cotton wax obtained as a by-product of a pilot plant operation in which 100-pound batches of Texas cotton fiber were extracted with hot benzene to obtain 25 pounds of wax from ten bales of cotton. The wax has a dark greenish-brown color, which changes to a tone of yellow when decolorized with activated carbon, fuller's earth, or a combination of the two. Without further refinement the wax has a characteristic disagreeable odor, and a consistency comparable with beeswax. The investigators report the following properties: melting point 68 to 70°; specific gravity, 15/15° 0.959; saponification value 70.6; acid value 32.0; ester value 38.6; acetyl value 73.1; iodine number 24.5; fatty acids 25 per cent; unsaponifiable 25 per cent; Hehner value 100 per cent; and Reichert-Meissl value 0.

The chemical composition of cotton wax has been intensively investigated, since some of its components are not to be found in any of the well known waxes. In 1923 Fargher and Probert[42] treated American cotton in sliver form with redistilled 90 per cent commercial benzene, heating it with superheated steam. Then by carefully treating the extract with selective solvents they obtained the alcohol, acid and hydrocarbon components. In this manner they discovered a new alcohol, $C_{30}H_{62}O$ for which they proposed the name of *gossypyl alcohol*. *Neomontanyl alcohol*, $C_{28}H_{58}O$, was present in a small amount, also *ceryl alcohol*, $C_{26}H_{54}O$, and *carnaubyl alcohol*, $C_{24}H_{50}O$.

The amyrins found in cotton and some other plant waxes are of the formula $C_{30}H_{49}\cdot OH$. They are derivatives of triterpenes, $C_{30}H_{48}$. These alcohols do not readily combine with the higher acids, but combine readily with ionizable acids, such as acetic, to form acetates. However they are found as palmitates and less often as myristates and stearates in plant life. α-Amyrin when crystallized from ethanol in fine long needles, melts at 183°. Its acetate melts at 220°; $[\alpha]_D$77.9. β-Amyrin crystallizes in long hard needles, m. 195°; $[\alpha]_D$ in $CHCl_3$ 87.8–88.4, in benzene 98.1. Its acetate melts at 235°; $[\alpha]_D$ in $CHCl_3$ 81.1. The amyrins when mixed show a eutectic at 181° and 77 per cent of the α-form.

Gossypyl alcohol, not to be confused with toxic principle, *gossypol*, is not identical with myricyl alcohol, and occurs in three forms—α, β and γ—of different melting points; they give identical derivatives when fused with potash lime, yielding the same acid. Gossypyl alcohol crystallizes from hot benzene in coffin-shaped needles, and from pure anilin in long thin blades. With a pyridene-anilin reagent it is precipitated as dianilin. The montanyl alcohol present on fusion gives montanic acid, identical to that in montana wax.

Form	Solubility (grams per 100 ml)		
	Chloroform (20°)	Ether (25°)	Ethyl lactate (25°)
α (m. 87–88°)	0.05	0.19	0.08
β (m. 86°)	0.55	0.43	0.07
γ (m. 82–83°)	0.64	1.09	0.09

γ-Gossypyl alcohol has also been found in the corms of the jack-in-the-pulpit, *Arisaema triphyllum*, (L) Schott.

Knecht and Allan,[70] by separating and acidifying the saponifiable portion of the wax, obtained *palmitic*, *stearic*, and a small quantity of an acid with a melting point of 74.4°. From the fatty acids of the saponifiable portion obtained from a secondary extraction with benzene they isolated an acid m. 70.8° in crystalline form, with a molecular weight of 455, which was thought to be myricinic ($C_{30}H_{60}O_2$). The presence of a still higher acid, $C_{34}H_{68}O_2$, was also indicated.

The acids in the free state include *palmitic*, *stearic*, *cerotic*, *montanic*, *gossypic*, and the acid $C_{34}H_{68}O_2$, known as geddic acid. Carnaubic, palmitic, stearic, oleic, and a lower isomeride of oleic acid occur as esters. The proportion of unsaturated to saturated acids is exceedingly small. The C_{34} acid present may be identical with that isolated by Schalfeef from beeswax, since it has the same melting point. Schalfeef was inclined to believe that melissic acid in beeswax was a mixture from which a C_{34} in the form of needles could be isolated. The alcohol corresponding to the C_{34} acid is *incarnatyl alcohol,* m. 72–74°, isolated by Sundwik[131] from bumble-bee wax, and by Rogerson,[117] of London, from the flowers of *Trifoleum incarnatum,* L., the carnation or crimson, clover.

The unsaponifiable portion of a benzene-extracted cotton wax (after removing petroleum ether extractable) yields a reddish-brown sticky wax, m. 63.4°, which contains *phytosterols.* Fargher and Probert[42] found that these phytosterols consist chiefly of *sitosterol* ($C_{27}H_{46}O$), and small quantities of α- and β-amyrin ($C_{30}H_{50}O$). Sitosterol also occurs as the corresponding glucoside, *sitosterolin.* Fargher and Higginbotham isolated from the wax of Egyptian cotton a different sterol from that found in American cotton, and identified this new sterol as phytosterol ($C_{29}H_{50}O$), which exists with the corresponding glucoside.

Cotton wax also contains about seven per cent of hydrocarbons. Knecht and Allan[70] obtained two hydrocarbons, one melting at 68.1°, and the other at 70°. These hydrocarbons were shown by analysis to be identical to *n-hentriacontane* and *n-dotriacontane.* Crystalline *triacontane* was later discovered by Fargher and Probert.[42]

The chemical composition of the wax as given below is based largely upon the results obtained by Fargher and others.

Phytosterols, Free and Combined as Esters: 12-14 per cent
sitosterol, $C_{29}H_{50}O$
stigmasterol, $C_{29}H_{48}O$

Pentacyclic Triterpineols, $C_{30}H_{50}O$: *3-4 per cent*
α-amyrin
β-amyrin
lupeol

Alphyl Esters of Wax Acids: 20-22 per cent
esters of mixed acids, m. 84°,
neutralization value 132, mean molecular weight 425

Free Acids: 8-10 per cent
cyclic-resin acids (small amount)
aliphatic, C_{16} to C_{34}

Free Monohydric Alphyl Alcohols: 42-44 per cent
ceryl, $C_{26}H_{54}O$
neomontanyl, $C_{28}H_{58}O$
gossypyl, $C_{30}H_{62}O$
geddyl, $C_{34}H_{68}O$

Hydrocarbons: 7-8 per cent
triacontane, $C_{30}H_{62}$ (small amount)
hentriacontane, $C_{31}H_{64}$
dotriacontane, $C_{32}H_{66}$ (small amount)

Glycerides, Glucosides, etc.: 1-2 per cent

Conrad[31] favors the removal of wax from either green lint cotton or white cotton by extraction with 95 per cent ethanol, and then transferring the wax to chloroform from the ethanol extractive which can be diluted with water to retain the sugar constituents. In 4 hours of the alcoholic extraction 0.61 per cent of wax was obtained for Egyptian cotton, and 0.72 per cent in 32 hours. The chloroform takes up sugar (mostly dextrose) only to the extent of 3 per cent of the total wax content of the cottons. Green lint cotton yields 13 per cent of wax by the Conrad ethanol-chloroform method.

Green Lint Cotton Wax. It has been recently reported by Conrad[31] of the U.S. Department of Agriculture that the lint from *Gossypium hirsutum*, a variety of Arkansas green lint, described by Ware of the Bureau of Plant Industry, differs from that of the ordinary strains of upland cotton not only in its bright green color and soft feel to the touch, but also in its remarkably high wax content. The wax content ranges between 14 to 17 per cent on the dry basis, contrasted with the 0.4 to 0.7 per cent of wax found in most cotton lints.

An experimental area of five acres has been under cultivation by the U.S. Department of Agriculture in South Carolina. Green lint cotton has been grown in the south for many years and is used for home spinning and handicraft work. Exposure of the green lint to sunlight converts it into a dull brown color. After removal of the wax, the fiber provides a high-grade cellulose.

The green lint cotton wax has been fractionated by means of 95 per cent of ethyl alcohol and ethyl ether, and the crude wax resolved into at least three fractions. The first fraction (30 per cent) was moderately soluble in alcohol, of a light green color, and showed a melting point of 85–90°. The second fraction (50 per cent) was slightly soluble in alcohol but freely soluble in ether, of a golden brown color, and showed a melting point of 86.5—90.0°. The third fraction (20 per cent) was only slightly soluble in both alcohol and ether, very dark brown in color, and had a melting point of 93–95°.

Conrad[31] noted the deep velvety green fluorescence of the third fraction in reflected light, and also studied the x-ray diffraction patterns of the wax, which he showed to be locked in the fiber. Conrad has not stated whether the wax contains gossypyl alcohol, which is found in three forms—α, β, and γ—in the ordinary cotton wax, but reports the absence of phytosterol.

Hemp Wax

Hemp wax is the wax of the bast fiber obtained from hemp, *Cannabis sativa*, L., indigenous to Asia, but now cultivated elsewhere as well. Obviously the bast fiber of *Musa textilis*, Nees, known as "Manila hemp," of

Hibiscus cannabis, L., known as "Deccan hemp" in South Africa, and other plants furnishing hemp also contain wax. The bast fiber of *C. sativa*, produced in Korea by steaming and scutching, has a length of 1.2–1.3 meters and is 0.6–0.7 mm in breadth on the average; it is light yellow in color. Its composition has been reported as follows: 9.77 per cent water; 2.07 per cent ash, 1.26 per cent oil and wax, 7.30 per cent water extractable, 71.03 per cent cellulose, and 10.64 per cent incrusting matter. On hydrolyzing the fiber with 1 per cent sodium hydroxide solution, 17.47 per cent was lost. The fiber consists of pecto-cellulose and ligno-cellulose.

The fatty substance, or oil and wax component, is brown and waxy-looking, and has a brittle conchoidal fracture. It has the following constants: d_{15° 1.019; m.p. 66–67°; acid value 46–47; ester value 145; iodine number 22–22.8; saponification value 162.6 (rising to 187–192 on prolonged treatment); and unsaponifiable (m.p. 60°, d_{15° 1.0022) 11 per cent.

In liberating hemp fiber from the stalks, the stalks are passed lengthwise through rollers to break them in longitudinal planes, prior to retting. A considerable amount of dust results from the mechanical operation, and this dust contains a lesser amount of fats, when extracted by benzene or other suitable solvent. In the production of paper pulp there is considerable offal. The wax from hemp dust has the following constants: m.p. 69°; acid value 22.2; saponification value 86.3; iodine number 33.3; and unsaponifiable 13 per cent.

Monti[106] extracted the powder formed in an Italian hemp works by means of trichloroethylene and obtained the following constants: d_{15° 1.001–1.003; m.p. 68–70°; saponification value 138, acid value 20.0. The wax was fractionated into the following portions: (1) ether-insoluble (40 per cent), probably a saturated alcohol; (2) soluble in ether and alcohol —free fatty acids of high molecular weight; (3) soluble in ether but insoluble in alcohol—esters and unsaponifiable matter.

Hemp wax is believed to consist of one or more monohydric alcohols, probably *ceryl alcohols*, monobasic saturated acids, together with esters and hydrocarbons. The melting point of hemp wax is a trifle higher than that of candelilla, and higher than that of flax wax.

Broom Wax

The tops of Holland broom, *Cytisus scoparius*, L., the Algerian broom, *Spartium junceum*, L., and other brooms contain fatty, resinous and waxy substances. This material amounts to about 2.5 per cent of the weight of the tops. The Holland broom extractable melts at 40° and contains 25.6 per cent of a wax with 64° melting point. The Algerian broom extractable contains 48.4 per cent extractable with a melting point of 64° also. The fibers of broom after retting and scutching are used to produce cordage and strong fabrics.

The lye used to boil broom to separate the fibers, when treated with sulfuric acid, yields a precipitate from which a fat and wax mixture can be extracted with solvent. The amount of this mixture is said to be proportional to the concentration of the lye and the boiling time.

Pisang Wax

Pisang wax is a wax derived from the leaves of *Musa simiarum*, Rumphius, and closely related species *M. corniculata*, Loureiro, and *M. acuminata*, Coll., all of Pisang. *Banana wax*, which unlike Pisang wax is not a commercial article, occurs as a coating on the under surface of the leaves, and the fruits and petioles of the banana tree, *Musa zebrina*, van Houtte, and *M. sapientum*, L., the common banana. The genus of Musa consists of gigantic herbs, the leaf stalks forming a trunk often more than a foot in diameter. The leaves of the species yielding Pisang wax are about six feet long. The fruit, which is banana-like, is dried and ground in the unripe state into banana flour, known as Guiana as "conquintay." *M. textilis*, Nees, produces hemp fiber. Musa seeds in East Africa Protectorate contain a white powder used as food by the natives.

The leaves of the species yielding Pisang wax are scraped with a knife by the natives in Java. They can scrape about one half kilogram of wax from each 100 kilograms of leaves. These scrapings are then thrown into boiling water; the wax melts and floats to the top of the water from which it can be collected. The wax is marketed in cakes that are white, cream, or greenish in color, and translucent. The wax is hard and easily pulverizable.

According to Gresshoff and Sack[134] the specific gravity is 0.963–0.970 at 15°; m.p. 79–81°; acid value 2–3; saponification value 109. The wax is soluble in boiling turpentine, amyl alcohol, or carbon disulfide. It is sparingly soluble in solvents such as alcohol, acetone, and ether.

The chemical composition of the wax has been given as an ester of a so-called *pisang ceric acid* ($C_{24}H_{48}O_2$) m. 71° and *pisang ceryl alcohol*, m. 78°. The former corresponds closely to the isomer of normal C_{24} acid, known as *carnaubic acid*, and the alcohol has the identical melting point of *ceryl alcohol*, isomer of n-hexacosanyl alcohol. Hence Pisang wax must consist chiefly of *ceryl carnaubate*, with a melting point of about 81°.

Tea Wax

A wax can be extracted from the leaves of the tea shrub, *Thea sinensis*, L., *T. japonica*, or *T. sasanqua*. Tea leaves contain wax, resin and fixed oil, the wax however being in the smallest amount by far less than 0.15 per cent. A specimen of tea wax may be found on exhibition at the Field Museum, Chicago; it is black in color, and of plastic consistency. Small quantities have also been offered from abroad to tea importers in New York.

Its composition is not fully known, but it is believed to contain *phytosterol* linked with *daturic acid,* and it is known to contain the mono-ethanoid alcohol, *nonenol* $C_9H_{17}\cdot OH$. Tea wax is capable of producing excellent emulsions, and if ever commercialized would probably be useful as an emulsifying wax in the food industry.

A wax is produced from the insect *Ceroplastes rubens,* Maskell, grown on the tea plant as a host. This wax has been described by Koyama as buff in color, hard but plastic and of 54–56° melting point. (See Ceroplastes waxes, p. 69).

Uva Ursi Wax

A wax is extractable from the leaves of the *Uva ursi,* L., a well known drug. The low evergreen shrub is commonly called "bearberry." If the leaves are extracted with ether, *ursolic acid* may be isolated. This acid is probably identical to that obtained from the skin of the cranberry, and has a melting point of 284–285°. The derivatives on methylation melt at 230° and 172° respectively, and the acid is thought to exist in α and β modifications, or isomers, which have almost identical melting points, in 290–291°, and 292–293° respectively. Ursolic acid of the *Uva ursi* was formerly known as urson.

(3) Waxes from Grasses and Sedges

Sugar-Cane Wax

Cane wax, originally called *cerosie* and more recently *cerosin,* is the wax found on the exterior of the cane-stem of the sugar cane, *Saccharum officinarum,* L. During the milling of the cane, a large portion of this wax, a powdery substance, becomes detached, and mixes with the expressed juice as an insoluble suspended impurity, the remainder of the wax being left in the bagasse, which is the waster after expressing the juice. The actual amount of wax in sugar cane is less than 1/10 of one per cent by weight, and most of this wax is near the nodes of the cane.

The following methods for the recovery of the wax have been proposed:

(1) *Extraction directly from the cane.* The stalks are propelled through a tank of hot water which is flowing in the opposite direction; while submerged the wax is separated and collects as a film on the surface of the water. This collected material is then allowed to flow into a recovery apparatus such as that described by Bunker.[24]

(2) *Extraction from the filter press cake.* The cake is first carefully dried, crushed to a powder, and heated with a suitable quantity of benzene. After settling and decantation, the hot benzene extract is filtered and allowed to cool. The wax separates out and is recovered by a second

filtration. This crude wax is very dark in color and must be purified. About half of the benzene-soluble matters in the cake consist of wax. As much as 10–12 per cent of wax on the dry basis is recoverable. A paraffin solvent, according to Clatcher, works out more economically than the proposed benzene solvent.

(3) *Extraction from the raw juice.* The raw juice before deliming or sulfitation is treated in centrifugal-subsiders, as proposed by Cross, and the suspended solid matters, including wax, are deposited in the drum, instead of passing into filter presses. The wax can be extracted from the centrifugal deposit by boiling with denatured alcohol, filtering and chilling out the wax.

(4) *Extraction from the bagasse.* The Simmons method calls for the extraction of cane wax at the time the bagasse sugar cane residues is converted into paper material. The bagasse is digested with sodium hydroxide under 12 to 30 lbs steam pressure, then washed, redigested with the caustic at 40 lbs pressure and again washed. The residual washed fiber is converted into paper, and the cane wax is extracted from the caustic solution by concentrating this to one-fourth of its volume and allowing the wax to rise to the surface as a scum. The scum is then removed by skimming ladles and purified in any convenient way. The yield is not over 0.5 per cent.

The only economical method thus far is the third one described; that is, on liming the juice the precipitated non-sugars carry down the suspended particles of wax, which thus pass into the sediments in the settling-tanks, and finally into the filter press cakes, containing the fiber, wax, and starch. The wax is then extracted from the filter press cake by hot paraffin solvent, such as a high boiling naphtha, and the wax deposits on cooling and can thus be removed from the chilled liquid. The yield is from five to seventeen per cent of crude wax.

In Natal the dry mud press-cake in plant operation established 1914–18 yielded 14 to 17 per cent of wax. It is reported that in 1924 the plant there produced 6000 short tons of a dark colored wax per annum for export. Wax has also been recovered on a commercial scale in Java. Wax has been produced in the province of Tucuman, Argentina; in East India; and on Cuban estates; as well as elsewhere, but not on a commercially profitable basis.

The crude wax consists of a soft part, containing fats and oils, and a hard part, consisting largely of unsaponifiable matter. The objective is to free the wax from the soft part, and thus obtain the more valuable true wax. The wax in the soft part melts at 60° or less, but the true wax from the hard part melts at 78–80°. Bleaching of cane wax is difficult. Soft wax separated from the hard melts at 60–62°, has an acid value of 47, and a saponification value of 177.

East Indian Cane Wax. East Indian cane wax is extracted from the dry filter press cake by means of a light petroleum solvent and with a yield of 10–15 per cent. Usually this is a greenish-brown hard wax which has analytical constants within the following range: melting point 66–67°; specific gravity 0.963–0.984 at 25°; acid value 12.0–23.4; saponification value 35.5–81.1; iodine number 16.2–31.5; acetyl value 55–60.7; unsaponifiable 62.3–80.0; Hehner number 83. The wax contains mixed sterols, brassica-, stigma-, and sito-. It has been reported that the wax from one central yields only stigma-, and sitosterols.

Rao and Gupta[113] recommended purifying cane wax by boiling the petroleum spirit (b. p. 120/130°) extract with five per cent of nitric acid and direct steam for twenty minutes, cooling, and washing the separated wax free of acid. In this way a slightly yellow-tinged white wax is said to be obtained. The wax has a melting point of 66° minimum when derived from East Indian filter press cake.

South African Cane Wax. Rindl,[116] South Africa, reported on a crude wax directly extracted from the press cake by means of benzine. The wax showed the following constants: melting point 55°, setting point 51°, density$_{100°}$ .968, acid value 38.6, saponification value 167.9, ester value 129, Hehner number 88.6, Reichert-Meissl number 7, iodine number 60, unsaponifiable 27.7 per cent. The wax contained glycerol 7.2 per cent, mineral matter 2.03 per cent, lecithin 2.7 per cent and nitrogen 0.15 per cent.

Taylor in 1919 reported on an examination of a well refined wax from the Uba variety of cane in Natal. The constants were as follows: melting point 71–73°, acid value 15.9, saponification value 98, ester value 82.1, iodine number 28.6, ash 0.6 per cent, unsaponifiable 55 per cent.

The crude wax extracted from the press cake of Cuban cane according to Bardorf[11] amounted to 21.2 per cent. The wax contained a soft part, olive-green in color, which melted at 52°; and a hard part, brown in color, which melted at 82° and was stable to heat. Eastwick states that a commercially purified cane wax melts at 60–62°, has an acid value of about 47, and a saponification value of 177.

The following are constants which represent the mean values obtained from numerous specimens of semi-refined sugar cane wax other than American: melting point 67°; setting point 60°; specific gravity 0.982 at 15°, 0.974 at 25°, 0.836 at 100°; acid value 24.6; saponification value 96.0; ester value 79.8; iodine number 34.5; unsaponifiable 47.5 per cent; Hehner number 86.3; acetyl value 58; Reichert-Meissl number 7.

The cane wax obtained by Cross from filter press cakes in the province of Tucuman, Argentina was of a greenish color and was much softer than the true cane wax, m. 60–70°. By fractional crystallization from benzine it was possible to separate the cane wax from the other constituents. The wax so obtained had a melting point 78–80° and after purification and recrystallization it melted at 81–83°. Suspended substances removed from raw juice by means of a large juice centrifugal yielded a product which upon one crystallization gave a pure hard wax with a melting point of 82°.

Philippine Cane Wax. A crude cane wax from the Philippines was brown in color, streaked with a great deal of green material, which contained much chlorophyll. Since the behavior of chlorophyll is not unlike that of fat-wax substances it is not easily separated. Attempts to saponify a portion of the wax led to serious trouble in separating the true wax ingredients from the emulsion. An attempt was then made to destroy the chlorophyll by boiling the crude wax with a 50 per cent solution of sulfuric acid and sodium dichromate. On cooling the wax separated at the top, whence it was washed with water, taken up in chloroform, and filtered through animal charcoal to yield a soft brown wax.[148] The latter semi-crude appeared to be quite identical to the original wax except that chlorophyll was absent, and any traces of sugar, minerals, or other soluble matter were thereby removed. The yield of semi-crude wax by this process was about 94 per cent.

	Crude Green Cane Wax	Pale Brown Cane Wax
Specific gravity at 25°	0.998	0.972
Melting point	52–70°	71.1°
Acid value	56.8	40.0
Saponification value	137.5	147.5
Iodine number	83.8	45.6

In another experiment the original crude wax was distilled under reduced pressure, and there resulted a pale yellowish wax of soft consistency. These soft waxes appeared to contain in part glycerides of unsaturated and saturated acids. By extraction of the crude wax with warm ethanol, then chilling and siphoning the crystal wax, and repeating the extraction and separation six times, there resulted a refined wax of pale green color and of a high degree of hardness like carnauba wax. Careful treatments with warm (not hot) ethanol removed the chlorophyll rather slowly, but easily removed the free fatty acids and the fats. Hanzely[148] obtained a melting point of 79.4° (174° F) for the purified product, which confirms that of Cross who gives 78–80° as the melting point for the true cane wax.

An attempt was made to free the original crude soft wax from chlorophyll, soft vegetable fats, and fatty acids by treatment with hot alcohol, chilling, and centrifuging out the crystals of wax. The product obtained was a pale moss-green colored wax, lustrous, fairly hard (durometer test

80 at 83° F), and brittle. It could be sun bleached. The constants on this semi-refined wax were: specific gravity 0.978 at 25°, melting point 77.2° (171° F), acid value 23.1, saponification value 95.0, and iodine number 19.8.

When the crude wax was heated on a dry hot plate for a prolonged time it was found that the chlorophyll could be destroyed. A fairly hard brown mass was obtained which consisted, half and half, of an alcohol-soluble and an alcohol-insoluble portion. The latter was completely soluble in chloroform. The constants for the brown mass and its components as separated by alcohol are given below:

	Hard brown waxy mass	Ethanol-soluble component	Ethanol-insoluble component
Specific gravity at 25°	1.013	0.983	0.949
Melting point	68.3° (155° F)	72.8° (163° F)	63.9° (147° F)
Acid value	46.5	21.6	7.2
Saponification value	148.0	126.7	136.6
Iodine number	44.5	44.5	58.4
Ester value	101.5	105.1	129.4

Both the soluble and insoluble portions are soft waxes about the same as a semi-crude cane wax. The ethanol-soluble component contains most of the fat acid and the *myricyl palmitate,* part of the *phytosterol,* whereas the *phytosteryl esters* as well as some of the *myricinic acid* remain in the insoluble component.

Louisiana Cane Wax. A refined sugar cane wax has been prepared from the large amount of accumulated tailings at the sugar refineries in Louisiana. It is of a greenish-brown color, lustrous in appearance, brittle, and ochre in color when subjected to fluorescent light.

In a pilot plant of Houma, the dry press cake from Oliver filters is made slightly plastic with water, formed into pellets, dried and extracted with toluene, benzene or light petroleum spirit; toluene being preferred because of the higher yield of wax. The amount of crude wax from the cake of 22 Louisiana factories varied between 5.3 and 16.3 per cent on the dry cake basis. The extract contains 3.6 to 12.9 per cent of hard wax and 1.8 per cent of fatty substances. In the western districts of the state the yield is 11.3 to 16.3 per cent. The fatty substances and the phytosterols and carotene are removable with acetone. The residual wax is lightened in color after treatment with an equivalent amount of charcoal. It is freed from acetone and dried.

This wax has a melting point (A.S.T.M.) of 77.7°, softening point 76.9°, ball and ring melting point 78.9°, solidifying (setting) point 72.2°. Its durometer hardness is 98 at 25°, 100 at 4°. The density at 15°/15° is 0.9969; at 25°/15° 0.9919; and at 100°/15° 0.8370.[149] A specimen of

Louisiana cane wax had an acid value 13.0, saponification value 57.0, and iodine number 7.96. The unsaponifiable matter was 17.5 per cent.

In sugar cane wax studies made by Balch and Broeg,[10a] the wax content of millable cane constituting the 1942 crop from Houma Station varied according to the location of the crushing plants. The average content of crude wax they found to vary between 0.114 and 0.241 per cent. The average content of hard wax varied from 0.058 to 0.165 per cent. The hard wax was found to constitute 51.0 to 68.6 per cent of the crude wax. In studying the wax removal from sugar cane by milling the average percentages obtained in the crude wax content of mill products, and computing same on the cane basis weight, the results were as follows: crusher juice 0.036 per cent, remaining juices 0.024 per cent, bagasse 0.086 per cent, giving a total crude wax content of 0.146 per cent. The average amount of wax removed by milling was 41 per cent.

The crude wax content of clarification mud press cake for the 1942 season at Houma ranged from 3.67 to 8.13 per cent on samples taken from 12 factories in the Eastern District, with a weighted average of 5.86 per cent. The weighted average on the moisture-free basis is 8.75 per cent. The wax content of the press cake in the Western District proved considerably higher, since samples taken from 7 factories showed a crude wax content of 2.53 to 4.10 per cent, with a weighted average of 10.22 per cent, or 13.57 per cent on the moisture-free cake basis.

Balch and Broeg have also found that the removal of fatty matter from crude wax to yield a hard wax may be accomplished in several ways. Two solvents, acetone and 2-butanone (methyl ethyl ketone) were compared critically. The latter solvent is more efficient than acetone in removing the fatty matter and the pigments, but it also has a higher solvent power on wax constitutents. About 5 per cent more hard wax remains after the treatment with acetone, regardless of whether the crude wax was originally extracted from the mud press cake with toluene or with petroleum naphtha.

In order to meet the trade requirements it becomes necessary to produce a lighter colored hard wax, since the ordinary hard wax is too dark in color. To obtain the highest yield of light-colored wax, toluene is preferred to petroleum naphtha for extracting the crude wax. Apparently most of the color of the hard wax remaining after removing the fatty matter which carries most of the chlorophyll and other fat-soluble pigments is associated with the fraction of the hard wax that is insoluble in boiling ethanol alone or in acetone followed by ethanol. In selecting a solvent for effecting this separation, it was discovered that 2-propanol (isopropyl alcohol) proved most satisfactory. The extraction may be easily made by digesting the hard wax, after the removal of the fatty matter, with about ten times its weight of alcohol under a reflux condenser until equilibrium is established. The green extractive can be removed by decolorizing carbon and permitting the wax to crystallize out and removing the mother liquor by filtration or other physical means. Louisiana wax is said to respond better to this purification treatment than the waxes of Cuba, South Africa and South America.

The yield of hard wax from the crude after freeing the latter of the fatty matter by acetone is 67 to 75 per cent, and the yield of light-colored wax, if derived from toluene-extracted crude wax, will average about 78 per cent.

Thorpe[134] states that the purified cane wax can be obtained by removing the portion soluble in cold alcohol—that is, the chlorophyll—then dissolving it in boiling alcohol, cooling, pressing, driving off the alcohol and melting. The purified wax is dull yellow, hard, and pulverizable.

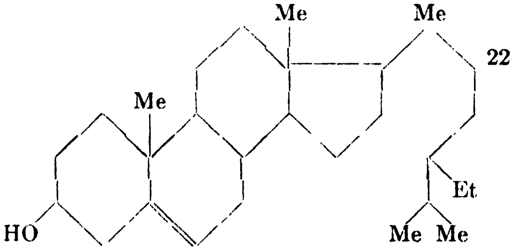
Properties of Cane Wax. Cane wax is partially soluble in cold alcohol, 5.9 grams dissolving in 100 ml U.S.P. ethanol (95 per cent) at 26°; and is partially soluble to a much greater extent in hot ethanol. Cane wax is partially soluble in ethylene dichloride, 1.6 grams dissolving in 100 ml at 37°. It is quite soluble in chloroform, but very sparingly soluble in cold ether. Hot ether dissolves it to some extent, depositing small crystal grains on cooling. It is soluble in hot amyl alcohol. The highly refined wax is reported as melting at 82° and solidifying at 80°, and has a specific gravity of 0.961 at 10°. When made into a taper it burns with a fine white flame like spermaceti.

In a crude cane wax there is a fairly large proportion of *caproic*, *palmitic*, *palmitoleic*, *stearic*, *oleic*, and *arachidic acids*, all of which are readily saponifiable. The non-saponifiable material consists of about 80 per cent of the higher alcohols, *triacontanol* or *myricyl alcohol*, about 10 per cent of a mixture of sterols, from which *brassica-*, *stigma-*, and *sitosterols* have been isolated, and about 5 per cent of *pentatriacontane*.

The chemical and physical constants of the cane waxes (cerosins) may be fairly well summed up as follows:

Grade	Color	M. P. (°C)	Sp. Gr. at 25°	D. Hardness at 25°	Acid Value	Sapn. Value	Iodine Number
Crude	olive-green	52–60	0.988–0.998	0	38–57	137–177	59–84
Refined commercial	green-brown	61–71	0.972–0.978	20–75	14–47	54–148	19–40
Double refined	dull yellow	77–82	0.961–0.979	75–85	8–23	55–95	13–29
Louisianan	light-brown hard	78	0.9915–1.000	98	13	57	8

Sterols in Cane Wax. Mitsui[104] reported in 1937 that on extraction with benzene or ether, the press cake from the manufacture of raw sugar yielded 8.3 per cent of wax; that from the manufacture of white sugar 2 per cent and bagasse 0.43 per cent. From 100 kg of the wax from the press cake could be obtained 2.0 kg of *stigmasterol* and 0.77 kg of *sitosterol*, $C_{29}H_{47}(OH)$. These were isolated in the tetrabromide and acetyl derivatives. In 1938 the same investigator extracted the unsaponifiable matter with acetone, and removed the precipitate formed in cooling. Light yellow plates were obtained from the filtrate, which were identified as *stigmasterol*. *Sitosterolin* was also isolated from the filtrate. Certain ketones as *trans-dehydroandrosterone* and unknown OH ketones were obtained from the dibromides by oxidation with chromic anhydride. The constitutional structural formula of *cane-sitosterolin* may be basically as follows:



Cane-sitosterolin (22-dihydrostigmasterol)

In 1939 Mitsui[105] removed the crystalline substances from cane wax with acetone, and extracted from the unsaponifiable a reddish-brown oil by treatment with cold methanol. By treatment of this extract with benzene a crystalline product m. 206° was obtained, and this had the formula $C_{29}H_{52}O_2$. It was named *α-saccharostanediol*. The yield was computed as 4 per cent of the wax. The mother liquor of α-saccharostanediol was kept at 0° and saturated with HCN. Sistosterol allophanate crystallized out. By treating the filtrate of the latter with acetone and methanol colorless scales m. 160° were obtained. The substance is named β-saccharostenone and has the formula $C_{29}H_{48}O$. The yield was 0.1–0.2 per cent of the wax.

Chemical Composition of Cane Wax. The chemical composition of a semi-refined sugar cane wax based upon its chemical constants would appear to be about as follows:

Wax Esters: 70–72 per cent
- myricyl palmitate, m. 73° (20%)
- myricyl myricinate, m. 86° (1–2%)
- phytosteryl esters of dihydroxy palmitic acid, m. 55°? (13%)
- stigmasteryl ester of palmitic acid (37–38%)

Glycerides: present

Free Fat and Wax Acids: 14 per cent
- palmitic acid (large amt.)
- myricinic acid (small amt.)
- palmitoleic acid (small amt.)

(Cont'd Over)

Alcohols: 12–13 per cent

- Monohydric:
    - myricyl alcohol, m. 87.5° (8%)
- Cyclic and Derivatives:
    - sitosterol, $C_{29}H_{50}O$ m. 138° (0.8%)
    - α-saccharostanediol, $C_{29}H_{52}O$ m. 206° (4%)
    - β-saccharostenone, $C_{29}H_{48}O$ m. 106° (0.1–0.2%)

Hydrocarbons: 3–5 per cent

- hentriacontane, m. 68°
- pentriacontane, m. 75° (1.5–2%)

NOTE: The above composition is based on a wax of 67° melting point, having an acid value 25, saponification value 80, ester value 55, and an iodine number of 29. The cholesteryl esters have been largely computed as stigmasteryl ester, stigmasterol, $C_{29}H_{47}OH$, being a sterol with two double conjugated bonds. The unsaponifiable matter amounts to 62.3%.

Utilization of Cane Wax. According to Rindl[116] cane wax has been used to a limited extent in the polish and electrical industries, for gramaphone making, and as a replacement for carnauba, beeswax, and montan wax in other industries. Samples of American wax of 174° melting point sent to the trade, according to Crowe, indicate there will be a good demand for the product whenever it is produced in quantity. Crowe states that it can be used in the manufacture of polishes, impregnated and coated products, moulded articles, and to replace vegetable waxes now difficult to secure.

A report in 1937 from the American Consul, John Corrigan at Durban, Union of South Africa, made to the U. S. Department of Commerce stated that up to the time of the revolution in Russia, the latter country was the principal market for the sugar cane wax produced in Natal, as it was utilized for the manufacture of candles used in the Orthodox churches in connection with religious services. Following the success of the Bolshevist revolution and the war on religion, the demand for the wax dropped rapidly; and as no markets other than this particular one could be discovered, the plants about Durban were forced to shut down, and since that time no cane wax has been manufactured in Natal. In making a substitution of beeswax in a candle formula less of the cane wax would be used, since the latter is harder and brittle, somewhat like candelilla wax. It was estimated by C. G. Smith & Company, Ltd., of Durban that it would require an expenditure of £10,000 to re-establish the plant of the principal producers in order to again produce the wax in volume. The wax was quoted by Smith at £30 per ton of 2000 lbs. f.o.b. Durban. The status of the industry in Africa has been reported through the courtesy of C. C. Concannon, Chief of the Chemical Division, Department of Commerce, Washington, D. C., on the basis of the rather meager consular reports available.

Crowe stated that the U. S. Dept. of Agriculture sees the possibility of recovering annually some 6 or 7 million pounds of wax from the "mud" obtained as a by-product in the clarification of the juice expressed from the Louisiana sugar cane. The mud yields 5 to 17 per cent of crude wax.

Bamboo Leaf Wax

A wax is derived from the leaves of a bamboo, *Sasa paniculata*, Makino, which grows abundantly in the mountainous districts of Central Japan. It is a brownish-yellow, hard, brittle wax resembling somewhat carnauba wax. Tuzimoto[135a] refers to the variety of bamboo as nemagari-dake, and was able to extract about one per cent of the crude wax from the leaves by means of petroleum ether. After a partial purification Tuzimoto determined the following constants for the wax: density $_{25^\circ}$ 0.961; melting point 79–80°; acid value 14.5; saponification value 43.4; iodine number (Wijs) 7.8; and unsaponifiable matter approximately 65 per cent. The wax contains high molecular fatty acids m. 81–82° and unsaponifiable matter m. 87–88°. Both *myricinic acid* and *myricyl alcohol* were identified in the wax, which components apparently exist combined as the ester, *myricyl myricinate.* Alcohols or esters corresponding to *montanic* and *cerotic acids,* are possibly also present, but there is no appreciable amount of sterols.

If it were possible to commercialize this wax there would be many uses for it, particularly as a substitute for carnauba wax.

Esparto Wax

Esparto wax is derived from esparto grass of Libya, or elsewhere in Northern Africa. Two species are cultivated for the utilization of cellulose, namely, *Stipa tenacissima*, L., and *Lygeum spartum*, L. The grass is shipped to Scotland where it is dewaxed so that it can be made into paper. Many of the fine grade papers in the British Isles are made from esparto grass. After the grass has been flailed the dust accumulated is sent by the paper mill to a central plant, which is practically the sole world producer of esparto wax. The amount of esparto wax available for sale is about 500,000 pounds per year; most of this being consumed in the British Isles in the arts and industries.

Esparto wax has the following characteristics: Specific gravities 0.9891 at 12°, 0.9880 at 15° and 0.8370 at 98°.[149] (The sp. gr. has also been given as 0.9940 at 15°, and 0.9900 at 25°.) The coefficient of cubical expansion is 0.000609 for the solid wax at 25°. The melting point (drop method) is 78.1°, solidifying point (setting point) 68.8°, liquating point 65.6°, acid value 23.9, saponification value 69.8, and ash 0.6 per cent. Solubility of esparto wax in ethanol 0.244 gram in 100 ml at 25°, and in ethylene chloride 1.48 grams in 100 ml at 37°.

Esparto wax is chemically composed of 15–17 per cent free wax acids, 20–22 per cent alcohols and hydrocarbons, and 63–65 per cent esters. The principal hydrocarbon is *hentriacontane* ($C_{31}H_{64}$ m. 68°). The acids include *cerotic, montanic, myricinic,* and *lacceric,* principally myricinic ($C_{30}H_{60}O_2$ m. 68°) lacceric ($C_{32}H_{64}O_2$, m. 70.5°) and hydroxy acids.

Esparto wax is a hard tough wax and provides a suitable economic substitute for carnauba wax in floor polishes, carbon paper, automobile polishes, furniture polishes, and shoe pastes. It blends well with other waxes. Normally the price of esparto wax is in the vicinity of twenty-five cents per pound.

Fiber Wax

Fiber wax is a commercial wax which is derived from some sort of grass straw, such as the esparto of Spain. Since the source of fiber wax is not always the same it varies in its physical and chemical constants. The wax of commerce is generally encountered in fairly large size pieces showing a conchoidal fracture, which are yellowish brown, brown, or dark brown in color. A softer wax is reported as melting at 61–66°. Hanzely[148] found a melting point as high as 80.5° (171° F) for a dark brown specimen, which had a hardness of 100 (durometer) at 25°. The specific gravity of fiber wax has been given as 0.968–0.988 at 15°. The chemical constants appear to be of the following order:

	Lighter colored softer wax	Darker colored harder wax
Acid value	16.5–30.0	10.6
Saponification value	61.0–76.0	67.2
Ester number	35.0–55.0	56.6
Iodine number (Hanus)	——	11.4
Unsaponifiable basis	67–72%	---

The addition of 2 per cent of fiber wax (80.5° m. p.) to paraffin raised the dry melting point from 54.4° to 57.7° (130° to 136° F), and the addition of 5 per cent to 75.5° (168° F). Fiber wax is used in the manufacture of shoe creams; also as a blending agent to produce high melting point artificial ceresin waxes.

Lachryma Wax

A wax is found on the stems of the *Coix lachryma,* L., a grass with a bony fruit. The plant is indigenous to the East Indies and Japan. The bony white seeds are called "Job's-tears"; they have some value as a medicine, and are used in China for food. They are sometimes made into necklaces. The plant belongs to the order Gramineae, and there are six species of *Coix* in tropical Asia. The wax is said to be similar to esparto wax.

Waxes of Other Leaf Blades

Leaf blades are found to contain sitosterols, higher alcohols, higher ketones, and higher hydrocarbons. The waxes extracted from these blades are exceedingly small in amount. Cocksfoot grass, *Dactylis glomerata*, L., a plant common in the United States, Canada and Europe, is reported to yield a wax consisting largely of *n-hexacosanol*, ($C_{26}H_{53}OH$, m. 79.5°) with less than 1 per cent of *tetracosanol.* The presence of *ceryl alcohol* has also been reported in bent grass, *Carex arenaria*, L.

The wax of the wheat blade, *Triticum aestivum*, L., is reported to contain *n-octacosanol* ($C_{28}H_{57}OH$, m. 83.4°) together with wax acids, and a hydrocarbon (m. 66°). The lucerne leaf, *Medicago sativa*, L., commonly known as "alfalfa," yields a wax containing *n-triacontanol* ($C_{30}H_{61}OH$, m. 86.5°) and *myristone* (m. 74–75°). It is estimated that the latter constitutes 0.17 per cent of the dry blade. Alfalfa seed yields a mixture of glycerides of palmitic, margaric, and stearic acids, but no wax. β-amyrin is found in both leaves and seed.

Straw from cereal grains when extracted with petroleum ether yields 1.8 per cent of a soft dark-green wax, which can be refined with activated charcoal to a light yellow wax with an 85.2 per cent yield. It has been found that cellulose prepared from wax extracted straw will bleach more readily.

The sisal-hemp, *Agave rigida*, Mill., of the Yucatan, cultivated in tropical countries and used as a substitute for hemp, contains about 20 per cent of wax in its cuticle according to Legg and Wheeler.[80] This wax yields 85 per cent of a mixture of wax alcohols, from which *montanyl* and *melissyl alcohols* have been isolated and identified.

The indigo plant, *Indigofera linifolia*, Retz., when extracted with alcohol yields an unsaturated lactone ($C_{26}H_{50}O_2$, linifolin, m. 95–96°) and a wax ($C_{42}H_{84}O_2$, m. 78–79°) which is a ceryl ester of palmitic acid (*ceryl palmitate*), in addition to tannins, phylobaphenes and glucose.[53]

(4) *Waxes from Broad Leaf Tree Leaves*

Wax of "Eucalyptus spp."

Leaves of trees which yield essential oils contain a slight amount of wax which can be recovered from the oil residues accumulating on prolonged storage. For example, wax is thus obtainable from the essential oil distilled from species of the Eucalypts. The greater number of some 200 species of Eucalypts in Australia are not commercially useful, but there are about 25 species which yield valuable essential oils consisting principally of eucalyptol and pinene. One of the preferred economic species is *Eucalyptus globulus*, Labill. (Fam. Myrtaceæ), indigenous to Eastern Australia and Tasmania, and cultivated in Southern Europe, California and the Southern United States. The mature leaves are collected, dried and steam distilled to obtain the volatile oil (3 to 6 per cent).

The wax was first isolated from the oil of *E. aceryula*, Hook., otherwise known as the "red gum" of Australia. Baker and Smith[10] gave the name *stearoptene* to the paraffin found. It melts at 55–56°, and they regarded it as a mixture of C_nH_{2n-2} homologs of higher melting point, such as *heptacosane* and *nonacosane*. The wax has been isolated since, from the oil of *E. paladusa* and from the oil of *E. smithii*, Baker. When purified the paraffin from the latter melted at 64°, which is the melting point of *nonacosane*. Aliphatic paraffins are not uncommon constituents of essential oils. Undoubtedly many other species of these evergreen trees would yield wax-containing oils.

Wax of Cacao Leaves

The leaves of the *Theobroma cacao*, L., growing from Brazil to Mexico, contain wax. One of the peculiar constituents of this wax is *β-amyrin palmitate*, isolated in 1892.

Wax of Sandal Leaves

In the order *Santalales* there are three families commonly known as the Mistletoe, Sandalwood, and *Balanophoraceae*. The mistletoe contains some wax in its leaves but most of the wax is in the covering of the berries (see p. 158). The leaves of the sandal, *Santalum album*, L., yield two unusual substances not generally found in plant waxes, namely *palmitone*, and *d-10-hydroxy palmitone*. The wax from the leaves contains but little fatty acid. The unsaponifiable according to Chibnall, *et al.* is:[27]

Primary alcohols: 50 per cent
  octacosanol (37½ per cent)
  triacontanol (12½ per cent)
Palmitone: 44 per cent
d-10-Hydroxypalmitone: 6 per cent
  m. 96.5, $\frac{17.5}{\mathrm{D}}$ 0.8

The plants of the family *Balanophoraceae* are tropical root-parasites and develop tuberous rhizomes and fleshy shoots which are yellow and without foliage leaves. Some of the species are rich in wax (see p. 145).

(5) *Waxes from Narrow Leaf Trees*

Waxes of Conifers

Bougault and Boudier[18] investigated the wax constituents of several conifers: *Juniperus sabina*, L., *Juniperus communis*, L., *Picea excelsa*, *Pinus sylvestris*, L., and *Thuja occidentalis*, L. They found that these waxes were largely mixtures of compounds belonging to a class of natural products having the properties of acids, alcohols and esters, and named them "*etholides.*" They provisionally assigned them the formula

$$RCH(OH)(CH_2)_nCO_2CHR'(CH_2)_nCO_2CHR''(CH_2)_n\ldots\ldots CO_2H$$

They isolated from the wax of the savin, *Juniperus sabina*, *juniperic acid* ($C_{16}H_{32}O_3$, m. 95°), which corresponds to oxypalmitic acid. They also isolated *sabinic acid* ($C_{12}H_{24}O_3$, m. 84°) an isomer of hydroxylauric acid.

The wax-like substances are extracted from the conifers by means of boiling alcohol (80 per cent), and purified by recrystallization from hot ethanol (95 per cent) after washing with ether to remove green coloring matter. The constants for the crude wax from *J. sabina* are: melting point 72–73°; acid value 40; saponification value 241; acetylized product with acid value 28.5, saponification value 260. *J. sabina* wax contains *juniperic*, *sabinic* and *thapsic acids.*

Crude wax from the pine, *Pinus excelsis* has the constants: melting point 75–78°; acid value 30, saponification value 227; acetylized product with acid value 28.5, saponification value 254. A crude wax obtained by extracting the young growing tips of the slash pine, *Pinus caribaea*, Morelot, with petroleum ether is reported to contain paraffins of the C_8 to C_9 range, a trace of α-pinene, *melissic acid*, *melissyl alcohol*, *nonacosan-10-ol*, a *sitosterol* and a *sitosterolin*, *palmitic*, *juniperic* and *behenic acids*, oily acids (probably *oleic* and *linoleic*) and *abietic acid.*

Wax of white-pine chermes of *Pinus strobus*, L., is believed to be an ester of *17-keto-hexatriacontanol*, m. 102°, and *11-keto-triacontanoic acid*, m. 103.4°. A similar ester of homologs is found in cochineal wax. The leaves of the Japanese pine, *Pinus thumbergii*, contain a wax-like substance showing the following constants: density$_{17°}$ 0.9201; melting point 78–80°; acid value 29.8; saponification value 218.9; ester value 189.1; saponification value after acetylation 219.2; iodine number 7.5. The wax contains *lauric*, *palmitic*, *stearic*, and *hydroxypalmitic acids*, possibly combined with ketonic alcohols.

Wax from the white cedar, *Thuja occidentalis*, has the following constants: melting point 76–84°; acid value 33; saponification value 221; acetylized product with acid value 33, saponification value 254. *Juniperic acid* is one of the wax constituents.

WAXES FROM FRUIT HAIRS

Kapok Wax

Kapok wax is a wax derived from the fruit hairs of Kapok, *Eriodendron anfractuosum*, DeCandolle. The plant is indigenous to tropical America, but is mostly grown in Java, and to a lesser extent in South Africa, the

Philippines, and the East Indies. The plant is of value for its lint and to some extent for the oil which is produced from its seeds. The hairs or lint are attached to the inner walls of the pod and not to the seed. The wax which appears to be of the academic rather than economic interest, may be prepared by solvent extraction of the lint, of which it constitutes about 5 per cent.

Matthes and Streicher[100a] of the University of Jena in 1914 reported on the physical and chemical constants of the wax, and have supplied information concerning its chemical composition.

The wax is a semi-solid which shows the following constants: melting point 240°, $n\,\frac{40^\circ}{\mathrm{D}}$ 1.4618, acid value 59.85, ester value 110.29, saponification value 170.14, iodine number 69.44, R-M number 2.02, Polenské value 0.97, unsaponifiable 28 per cent. It yields 15 per cent *palmitic acid* and 85 per cent liquid acids: *oleic, linoleic,* and *linolenic.* It is believed to contain *melissyl alcohol,* a hydrocarbon (possibly *eicosane*), and *phytosterols.*

Waxes from Roots and Rhizomes

Wax of Dandelion Root

The common dandelion, *T. taraxacum,* L., contains a wax in its root. The wax is recorded as having the following constants: melting point 152°; acid value 17.8; saponification value 114.9; iodine number (Wijs) 25.8; optical rotation $[\alpha]^{6}_{\mathrm{D}} = +47.2^\circ$ (which is the rotation given by taraxasterol). Stigmasterol and β-sitosterol have been isolated from the dry root.

Wax from Alkanet Root

A wax is obtainable, according to Betrabet,[15] from the root of *Anchusa tinctoria,* Lam. The powdered alkanet root is extracted with petroleum ether, the extract is evaporated and then treated with acetone, leaving behind a reddish-white wax. By refluxing with hot methyl ethyl ketone and bone black for four hours, and then concentrating the filtrate, white flakes of wax are obtained which when crystallized from ethyl acetate melt at 78°. The yield is about 0.2 per cent from the powdered root. The constants for the wax are as follows: $\text{density}_{30^\circ}$ 0.9676, $n\,\frac{80^\circ}{\mathrm{D}}$ 1.438, saponification value 69.2, acid value 12.9, unsaponifiable matter 58.6, iodine number 12.2, m. wt. of mixed acids 380. The wax when saponified with sodium hydroxide yields *carnaubyl alcohol* after evaporation of the soap and recrystallization of the residue from ethanol. The carnaubyl alcohol melts at 68°. On oxidation with chromic oxide and acetic acid it yields a white solid m. 72°, identified as *carnaubic acid.* Hence, the wax is chiefly carnaubyl cerotate. The wax is obtainable as a by-product when extracting alkanet root for its coloring principles.

Wax of Gentian Root

Wild gentian root, *Gentiana lutea*, L., growing in Sicily has been found by Binaghi and Falqui to have a wax principle. The fresh root was pulverized, digested with five times its weight of 95 per cent ethanol, the extract evaporated in vacuo, and the residue extracted with cold petroleum ether and evaporated, thus yielding a yellow-red oily residue weighing 3.4 per cent of the root. This residue was saponified with alcoholic potassium hydroxide and extracted with ether after removal of the ethanol. On dilution with water a wax appeared. This wax when crystallized from ethanol had a melting point of 142–143°, was soluble in chloroform, benzol, etc. The waxy principle is referred to as *gentiosterine.*

Balanophora Wax

The plants of the family *Balanophoraceæ* are indigenous to tropical or sub-tropical regions. They are root parasites. *Balanophora elongata* of Java grows on the roots of Ficus and other plants, and contains a large quantity of wax and resin. The torus of the flower of *Langsdorffia hypogœa*, Martius, of tropical America is edible. The plant is rich in wax and in New Granada it is sold under the name of "siejas" and burnt like a candle. The plants are very small, 5 to 6 cm long, and are so rich in wax that when set on fire they burn with a luminous flame. The natives make a paste from the plant and coat the ends of wooden sticks with it, for use as torches.

The wax may be extracted by boiling it out of the plant, the wax that melts and floats on the surface is either skimmed off and strained, or allowed to concrete as the liquor cools, and then removed. It may also be extracted by means of a suitable solvent.

The wax has the color of yellow beeswax and is of similar consistency. It melts below 100°, and has a density of 0.995 at 15°. It is soluble in ether and sparingly so in ethanol. The wax will dissolve in cold sulfuric acid from which it may be reprecipitated by water. It is a resinous wax and contains glycerides.

Root Fats. The so-called root fats are glycerides, and therefore do not fall in the category of waxes. Tropical sedge, poke root, senega root, etc., have oleic, palmitic, and linoleic as major component acids, and stearic and arachidic as minor components. About 80–90 per cent of the acids of root fats and oils are unsaturated, and the remaining 10–20 per cent are saturated and consist principally of palmitic acid. Constituents of root fats are *palmitin, olein,* and *linolein.* Ultée found the wax of the tuber of the balanophora to contain *palmitic acid* combined with β-amyrin, m. 195°, the ester having been named *balanophorin* by Göppert in 1841.

WAXES FROM BARKS

Many barks contain waxy material, usually in minute quantity. But few barks can be used to produce wax in commercial amounts; the Douglas fir bark perhaps shows the most promise since it contains much wax, and there are large quantities of this bark in the waste at the American Douglas fir lumber mills in the Northwest that can be utilized for this purpose.

Zellner[150] found that the bark of the privet tree, *Ligustrum vulgare*, L., yielded waxy matter containing *ceryl palmitate, ceryl alcohol,* a palmitic ester of an alcohol ($C_{23}H_{40}O$ or $C_{25}H_{44}O$, m. 215°); *phytosterol;* possibly esters of *behenic* and *arachidic* acids; platanolic acid. From the bark of the elder tree, *Sambucus nigra,* L., he obtained an alcohol ($C_{23}H_{40}O_2$, m. 216°); and another ($C_{27}H_{48}O$, m. 179°). From the bark of the alder tree, *Alnus viridis,* L., he obtained *ceryl alcohol;* an alcohol $C_{33}H_{60}O_2$, called *alniviridol,* m. 194°; and an alcohol $C_{24}H_{42}O_2$, m. 250°.

Beech Bark Wax

According to Clotofski,[29] a wax is extractable from beech bark, *Fagus sylvatica,* L., by triturating the ground bark with hot methanol. When the extract is cooled, there can be filtered off an insoluble portion consisting of paraffin m. 63–65° (probably *nonacosane*); a wax which on saponification and distillation *in vacuo* yields an alcohol $C_{20}H_{48}OH$, m. 73°; and an acid $C_{20}H_{40}O_2$, m. 56–57°, purified by lead salt. If water is added to the soluble portion an insoluble portion arises, which when treated with sodium carbonate yields waxy materials: *arachidyl alcohol* m. 72.5–73°; Hess *phytosterol* m. 132°; another sterol m. 225–227°; an acid $C_{24}H_{48}O_2$, m. 70–71° (*carnaubic acid* ?); and resin acids. Zellner found a ceryl ester of an acid ($C_{20}H_{40}O_2$, m. 80°, with acid value 179.4) and *phytosterol* as constituents.

Cork Wax

The outer bark of the cork tree, *Quercus suber,* L., indigenous to Southern Europe and Northern Africa, which yields the common cork of commerce, contains 5 to 10 per cent of a waxy material sometimes referred to as cork wax. The wax can be extracted from the cork by means of a suitable solvent, *e.g.,* ethyl acetate, but is soft and impure and the extractive requires purification to isolate the waxy bodies. Scurti and Tammasi[124] at Turin, isolated the waxy component *cerin.* Drake and Jacobsen[36] found that upon further refinement this cerin proved to be a hydroxy ketone crystallizing out in white needle-like laths, m. 247–251°; they gave it the empirical formula, $C_{30}H_{50}O_2$. In the mother liquor Drake and Jacobsen recovered another ketone, *friedelin*, which crystallizes out in white broad laths, m. 255–261° and has the composition $C_{30}H_{50}O$. Cerin and friedelin are polycyclic compounds belonging to the polyterpene group, and are quite stable. These triterpenoids can be seen in the cork cells under high magnification.

According to Zetsche and Lüscher[151] the hydroxy ketone and ketone constitute 18 to 19 per cent of the cork wax. The wax crude contains 10 per cent of sterols, including *phytosterol*, and 2 per cent of an alcohol $C_{24}H_{42}O_2$. The acids of cork were first observed by Höhnel in 1877; one called *phellonic acid* ($C_{22}H_{42}O_3$, m. 96°) was isolated by Kügler, and two others, *suberinic* ($C_{17}H_{30}O_3$, semi-liquid), and *phloionic* ($C_{11}H_{21}O_4$, m. 121°), were found by Gibson.

Schmidt considered *phellonic acid* as a cyclic acid. Drake[36] showed that phellonic acid, m. 93–93.5°, is 22-*hydroxytetracosanic acid*. It constitutes about 0.5 per cent of the cork wax crude, but more than half the fatty acids in the cork. Cork contains 28–40 per cent of total fatty acids. Scurti and Tammasi[124] had previously reported a phellonic acid identical with *α-hydroxybehenic acid*; that *suberinic acid* was *ricinoleic*, and *phloionic acid* of cork was a tricarboxyl aliphatic acid containing 25 C atoms, later identified as $C_{22}H_{43}(COOH)_3$, having white needles m. 121°, Cooke[32] lists the fatty acids in cork as follows: *phellonic* ($C_{22}H_{44}O_3$, m. 96°), 1,20-*eicosandicarboxylic acid* ($C_{22}H_{42}O_4$, m. 123.5–124.5°), *phloconolic* ($C_{18}H_{36}O_5$, m. 104°), and *phloionic* ($C_{18}H_{34}O_6$, m. 124°).

Zetsche and Lüscher[151] found *phytosterol* in the sterols of cork wax but only to the extent of 0.6 per cent. They also reported small percentages of *arachidic*, *oxyarachic*, *oleic*, *linoleic*, *cerotic*, as well as *phellonic acid* as constituents in the waxy matter. It is not unlikely that all three hydroxy acids—C_{20}, C_{22} and C_{23} may be found in cork.

Curcas Wax

Curcas wax is mentioned by Lewkowitsch as occurring on the bark of *Jatropha curcas*, L. The seeds of this plant by hot pressing yield curcas oil, an oil of some economic importance to Cape Verde Islands and other Portuguese colonies. In the West Indies and in South America the tree is known as the "purging-nut tree," and the seeds as "piñon." The wax consists chiefly of *melissyl alcohol* and *melissyl melissate*. The oil is used in Portugal for soap making, as an illuminant, and as a lubricating oil, for which purpose it is not particularly suited. In medicine the oil is used as a purgative. The wax has not been commercially exploited.

Birch Bark Wax

The wax of the bark of the birch, *Betula spp.*, L., contains the principle, *betulin*, m. 251° in as high as 10 per cent yield. Betulin is analogous to the amyrins, $C_{30}H_{49}(OH)$ and is believed to be $C_{30}H_{48}(OH)_2$.

Douglas Fir Wax

The bark of the Douglas fir, *Pseudotsuga taxifolia*, Lamb, of the family *Pinaceae*, indigenous to a region from Puget Sound to California, yields a wax in fairly large amount. This wax is interspersed in the corky layers of the bark, and is accompanied by resinous matter.

By hexane or other suitable solvent the wax can be extracted to the extent of 10–15 per cent of the weight of the bark. The crude wax is of a reddish-brown color, aromatic in odor, and is firm in consistency, showing a hardness by durometer of 83 at 25°. The wax has an acid value 80–81.5, saponification value 178–200, ester value 96–120, and iodine number 60–65. It melts at 63° (145.4° F). The wax contains an ester of melissic acid and an unsaturated alcohol, together with free *melissic acid.* The presence of *phytosterol* is indicated, as well as resin.

Oleander Bark Wax

The sweet oleander, *Nerium odorum*, Aiton, of India, yields an active principle known in Bengali as "karavi," a strong poison producing a powerful depression of the heart. The bark also contained a crystalline wax of a peculiar composition. The wax was crystallized by Pendse and Dutt[109] from boiling absolute ethanol and appeared as colorless glistening prisms of the following properties; melting point 97°, density 30°/40° 0.9804, saponification value 53.2, iodine number 16.2, acid value 16.8, and unsaponifiable matter 62.4 per cent. Hydrolysis of the wax gave an acid m. 93–94° (*cocceric acid*, m. 92–93°), and an alcohol m. 69° (*carnaubyl alcohol* m. 68–70°). It hence appears to be *carnaubyl coccerate.* The leaves of the oleander are reported to contain *tetratriacontane*, $C_{34}H_{70}$, with a melting point of 70–71°.

Ocatilla Wax

Ocatilla wax is a wax obtainable from the bark of a thorny tree or shrub, *Fouquiéria splendens*, Engelmann, known commonly, as ocatilla, or coach-whip cactus. *Fouquiéria* is a genus of the family *Tamariscaceae*, it is also reported as derived from *Moquinia hypolenca*, D.C., growing wild on the coast of the Rio Grande. All of the species are thorny shrubs.[134] They are commonly called candlewood, and grow in New Mexico, West Texas, Southern California, and Mexicò. The bark of *F. splendens* is said to yield 9 per cent of wax, whereas *M. hypolenca*, according to Lewkowitsch, yields but 2 per cent of wax for the entire plant, the bulk of which is contained in the leaves, the stem and stalks yielding a small proportion.

For the extraction of the wax the ocatilla plant is dry heated until the moisture is driven out, whereupon a shellac-like gum separates from the wax, and the wax is extracted by a suitable solvent such as benzine, and the solution evaporated to dryness.

Kraemer describes the wax as resembling beeswax, and in some respects its chemical composition is similar thereto. Ocatilla wax melts at 84°, and has a density of 0.984. It is soluble in alcohol and in benzene. Lewkowitsch determined its constants as follows: acid value 58.1; saponification value 185.0; unsaponifiable (m. 64–66°) 43.1 per cent; fatty and wax acids (m. 60°) 23.9 per cent. It is composed largely of *melissyl alcohol* and *cerotic acid.*

Little seems to be known of its uses. Its physical properties and chemical composition indicate that it could be exploited commercially if obtainable in sufficient amounts. Ocatilla gum has been used as a base for licorice chewing gum.

Mudar Bark Wax

The stem bark of *Calotropis gigantea,* L., which tree or shrub is called in northern India by the name of "mudar," and in southern India, "yercum," contains both resin and wax. Murti and Seshadri[106b] extracted the powdered freshly dried bark with ligroin, and then with ether to obtain 150 g of extractive from 4 kilos of bark. The extractive when boiled with a liter of alcohol for three hours and then cooled to 60° yielded a supernatant liquid, which when decanted from the insoluble viscous residue, deposited about 40 g of a white waxy solid. This white solid when recrystallized from ethanol and then from ethyl acetate, gave 20 g of wax with a melting point of 87°. The yield is ½ per cent of the original weight of the bark. The wax was found to consist of C_{31} and C_{32} hydrocarbons, a C_{30} acid and its near homologs, β-amyrin, and unidentifiable. The unsaponifiable portion melts at 65°, and at 69° upon recrystallization.

Wax is not only found in both the stem and root barks of *C. gigantea,* but in its latex. Most trees or shrubs with a milky juice, such as *Alstonia scholaris,* L. of the East Indies, source of the alkaloidal Dita bark of commerce, and many others, contain (besides lupeol-like compounds, α- and β-amyrins, and sterols) a small amount of wax which evidently is an associated end-product of their metabolism. (See waxes from latex trees, p. 150.)

Waxy Matters in Miscellaneous Barks

The following have been reported by Zellner[150] with the names of various investigators:

Plant	Alcohols	Sterols	Acids	Unidentified
Sycamore (*Acer pseudoplatanus, L.*)	ceryl	phytosterol	—	—
Hawthorne (*Crataegus oxyacantha*, L.)	ceryl	phytosterol	stearic palmitic	$C_{30}H_{50}O$, or $C_{31}H_{50}O$
Spruce (*Picea excelsa*, L.)	ceryl	—	stearic palmitic	(lupeol?) and other compounds
Purple willow (*Salix purpurea*, L.)	ceryl	phytosterol	palmitic stearic	a hydrocarbon
Locust tree (*Ceratonia siliqua*, L.)	—	—	palmitic stearic	
Spindle tree (*Euonymus europaeus*, L.)	ceryl	—	palmitic stearic	
Tree of Heaven (*Ailanthus glandulosa*, Desf.)	ceryl	—	palmitic stearic	a hydrocarbon
Elm (*Ulmus campestris*, L.)	—	phytosterol		$C_{27}H_{46}O + H_2O$ (m. 134°) $(C_{12}H_{24}O)_n$ (m. 74–75°) $C_{11}H_{20}O_2$
Horse chestnut (*Pavia rubra*, Larn.)	ceryl	sitosterol	—	a hydrocarbon

NOTE: The barks are extracted with petroleum ether and the alcohols isolated from the unsaponifiable, the acids being determined from the saponifiable. Many of the bark waxes undoubtedly contain amyrins; α-amyrin, β-amyrin, or lupeol.

WAXES FROM LATEX TREES

Cow Tree Wax

Cow tree wax[134] is a wax which is derived from a tree known as the cow-tree, milk tree, *pale de vaca, arbol de léche.* It is a species of *Brosimum* family order *Artocarpaceæ,* which consists of about eight species of trees with milky sap, indigenous to tropical America. One of these species, *B. alicastrum,* is found in Jamaica, where the seeds are called "bread-nuts" and are esculent, the milk juice being acrid. Another species, *B. galactodendron,* Don., is generally described as the source of the wax. The latex of this tree was separated by Justo Gomez into rubber, a wax melting at 64–65°, and α-amyrin m. 183°, the same amyrin as that obtained from gum elemi. Closely related to *Brosimum* is the genus *Clusia,* L., which is of the family order *Guttiferaceae,* and of which there are 65 species in tropical America. The cow tree of Venezuela has been referred to this genus by a French botanist. There is one species of *Clusia* in the United States, *C. flava*, Jacquemont, known as "wild mango," which has a resinous exudate used like pitch.

The cow tree wax derived from the tree growing in the north of Venezuela, near Lake Maracaibo, yields a wax which is marketed in Caracas. The tree yields a thick milk when incisions are made in the trunk. The milk when heated forms a skin; the skin is removed, and an oily liquid obtained upon evaporation. When the oily liquid is solidified it yields a yellowish-white, hard, translucent wax. The wax softens at 40°, melts at 50–52°, but not completely until 60°. The wax is saponified by caustic potash; it dissolves readily in essential oils, and in boiling alcohol, but redeposits on cooling. The natives use it as an ointment. The coagulated residuum of the latex is used in the manufacture of chewing gum. It is plastic at 37° and brittle at lower temperatures.

The sap of the cow tree, *Tabernaemontana sphaertcarpa*, Bl., contains both α- and β-amyrins., as does also the sap of *T. utilis*, Arn., of British Guiana.

Gondang Wax

Gondang wax or Godang wax is a wax which has gone under other names such as Kondang, Getah, Java, and, more commonly, fig tree wax. The fig belongs to the family order *Moraceae*, and there are about 650 species of the genus *Ficus* in the warm and tropical regions. The wax obtained in Java is generally ascribed to *Ficus variegata*, Blume; that obtained in Sumatra and Ceylon to *F. ceriflua*, Jungh, and is probably the same thing. There are other species producing wax but not in commercial quantities. One of these is *F. alba* which produces a latex that contains large quantities of wax, of what appears to be a stearate, as stearic acid is formed on hydrolysis. Ultée[138] reported the presence of *β-amyrin* and *lupeol* (free, and identified through its acetate and benzoate). There is but little rubber present in the sap. The wax melts at 60°. *F. elastica*, Roxburgh, the latex source of East Indian rubber, contains quantities of a different kind of wax.

Gondang wax is fairly hard, grayish brown in color, yellowish internally, with conchoidal fracture and friable, prepared by heat treatment of the latex. In its general character Gondang wax[139] is intermediate between wax and caoutchouc. The crude wax melts at 60° to a very viscous mass which on cooling remains viscous for a long time, and some aqueous liquid separates out. Its density at 15° is 0.963 (Wiesner) or 1.10115 (Gresshoff and Sack). It softens at 45°, melts at 56–57°, but is not perfectly melted at 73°. It will solidify at about 51°. The wax is soluble in benzene, chloroform, carbon disulfide, oil of turpentine, ligroin, and boiling alcohol.

A purified form of the wax may be prepared by dissolving the remelted crude in boiling alcohol; a white crystalline product is deposited on cooling which melts at 61°. Greshoff and Sack[134] found this to be an ester, $C_{30}H_{52}O_2$, of an alcohol ($C_{17}H_{28}O$, *ficoceryl alcohol,* m. 198°) and an acid ($C_{13}H_{26}O_2$, *ficoceric acid,* m. 57°). Possibly some free *ficoceryl alcohol* exists in the crude wax.

It has, however, since been shown that ficoceryl alcohol is the same as β-amryin. If the sap is coagulated by warming, or by the addition of alcohol, and the wax separated is then extracted repeatedly by a large volume of boiling alcohol, on cooling a product settles out that has a melting point 60–64° which if saponified with alcoholic potassium hydroxide yields an alcohol m. 197.5° identical with β-amyrin. Components of the wax are also lupeyl acetate and ficocerylic acid (probably closely related to palmitic). The wax melts at 69.5° and, according to Ultée, consists chiefly of *β-amyrin palmitate.* A synthetic ester prepared from β-amyrin and palmityl chloride melts at 77°, and differs little from the natural ester of Gondang wax.

Gondang wax is used as a candle material in Java and Sumatra.

Wax of Ficus Fulva

Ultée[137] in 1922 reported that the latex of *Ficus fulva,* Reinw., contains large quantities of a wax, which on hydrolysis, yields *stearic acid.* There is but little rubber present. *Ficus elastica,* Roxb., source of the East Indian rubber, contains much smaller quantities of a different wax in its latex. The stearic acid is combined with amyrins. The amyrins are ordinary constituents of lattices; for example the common silkweed, *Asclepias syriaca,* L., contains both α- and β-amyrins.

Ultée[138] reported that the coagulation of *Ficus alba,* Reiner, consists chiefly of a wax, m. 60°, and which on hydrolysis yields stearic acid, β-amyrin and lupeol. The β-amyrin was isolated free and in the form of an acetate, and the lupeol as a benzoate.

WAXES FROM FRUITS AND BERRIES

Japan Wax

Japan wax is usually defined as a fat contained between the kernel and outer skin of the berries the fruit of a small sumac-like tree, *Rhus succedanea,* L., which is cultivated in Japan and China for the wax it yields. The berry is of the size and shape of the common white bean. The wax occurs as a greenish coating on the kernels. In Japan the *Rhus succedanea* is known as yama-haze, and the *R. vernicifera* as uroshinoki, or lacquer plant. The latter grows in China, Indo-China, and India as well as in Japan. There is still another wax yielding species, *R. sylvestris*, which flourishes in the western provinces of Japan.

The principal production region of japan wax is in the island of Kyushu.[5] The trees are 20 to 30 feet high, beginning to bear the fruit kernels at 15 years, and continuing to do so for over 100 years; yielding 30 to 150 pounds of nuts per year. The trees, particularly *R. vernicifera*, are cultivated for the sake of the lacquer they exude, and japan wax might in this sense be considered as a by-product of the lacquer industry in the Orient.

The berries or nuts of *Rhus succedanea* are gathered, dried, crushed, and the kernels separated by winnowing. The kernels are steamed and placed in hempen cloth bags, steamed again, and pressed in a wooden wedge press. They yield about 15 per cent of a coarse, greenish, tallowy mass. In the pressing the flow of the last portion of wax is sometimes accelerated by the addition of a little perilla oil. The crude wax, solidifying at 50°, is cast into round moulds holding one pound each. In the usual refining, the wax is mixed with decolorizing carbon of vegetable origin, and water, and boiled thoroughly and then poured into cold water to form "wax flowers." The yield is about ten per cent of the original weight of the berries. The wax flowers are skimmed off, exposed to the sun for about twenty days, and the process of making flowers and sunning repeated, and the wax remelted and cast into cakes. It is then very white and opaque, and differs in appearance from other white waxes in opacity and freedom from gloss.

The purified wax which has not received the repeated sun bleaching comes to market in straw-yellow flat cakes, discs or squares. It is unctuous to the feel, somewhat rancid in odor like tallow, and it also has a rancid taste. Under ordinary circumstances it fuses at 51° to 55° but a recently solidified sample melts at a lower temperature. Its solidifying point is about 41°; the temperature rising to 48° or 49° in the act of solidification.

The specific gravity of japan wax at 15° is about 0.990, while in the molten state (98°) it is 0.875 to 0.877, compared with water at 15.5°. Thus, in the solid state it agrees in specific gravity with the true waxes, and in the molten state it is considerably heavier than the true waxes or the ordinary vegetable fats.

Kleinstück found that the specific gravity of japan wax approximates that of water, and, coupled with a high coefficient of expansion, gives rise to the peculiar phenomenon of its floating in water at temperatures of about 18° and sinking below 15°. He found the specific gravity to be 1.0074 at 7.2°; 0.9985 at 17.5°, and 0.9862 at 26.5°; when compared with water at 4°.

Japan wax has a saponification value of 206.6–237.5, an iodine number of 4.5–12.8, and a Hehner number of 90–91. The combined fatty acids have a titer of 58–59°, and a melting point of 56°–62°. The free fatty acids constitute 3–15 per cent (calculated as palmitic), and the nonsaponifiable matter constitutes only 1–1.6 per cent.

The chemical constitution of Japan wax or tallow has been a subject of almost never-ending study. In 1908 Schall[121b] studied its constitution, by hydrolyzing and distilling the free acids, and fractionating in the vacuum of a cathode light the undistilled portion, not volatile at 250° and 15 mm pressure. He obtained one per cent of dibasic acids which were carefully identified, and which later became known as *japanic acids*. These acids are *hepta-*, *octa-*, and *nonadecandioic*; that is $(CH_2)_{17}$, $(CH_2)_{18}$, and $(CH_2)_{19}$-$(COOH)_2$, the latter being specifically termed japanic acid by Beilstein. Japan wax, according to Schall, consists chiefly of *palmitin*, and free *palmitic acid*, $H(CH_2)_{15} \cdot COOH$, and a small amount of the japanic acids, which are believed to be intermediate products in the growth of the plant. The wax contains 10–14 per cent of glycerine in the combined state.

In 1910 Matthes and Heintz[100] obtained from the unsaponifiable matter of Japan tallow (1) about 60 per cent unsaturated oxygenated liquid products; (2) *myricyl alcohol*, m. 88°; (3) *phytosterol* with a double linkage, m. 139°; (4) *ceryl alcohol*, m. 79°; (5) saturated alcohol, m. 65°, apparently $C_{19}H_{40}O$. In 1935 Tsujimoto gave the component fat acids of unbleached wax of *Rhus succedanea*, free from kernel oil, as 77 per cent *palmitic*, 5 per cent *stearic* plus *arachidic*, 12 per cent *oleic*, a trace of *linoleic*, and 6 per cent *dibasic acids* (6.2 per cent in "tsuta-urushi" wax and only 1.6 per cent in "yama-háze"). He states that *myristic*, *hexadecenoic*, *linolenic*, and volatile lower acids appear to be absent. The dibasic acids are separated from the monobasic acids by virtue of their difficult solubility in petroleum ether. Tsujimoto gives the dibasic acids a higher formula weight than Schall, *e.g.*, *docosandioic acid*: $(CH_2)_{20} \cdot (COOH)_2$, m. 125.7–126.3° (Sitiro Siina) and *tricosandioic acid* $(CH_2)_{21} \cdot (COOH)_2$, which is the main constituent.

Tsujimoto states that when a petroleum ether extract of japan wax is filtered through japanese acid clay the dibasic glycerides are preferably adsorbed in the clay, from which a glyceride mixture containing 24 per cent dibasic acids can be recovered. From the filtrate was obtained a white, brittle solid containing no dibasic acids. When the glyceride mixture is crystallized from hot absolute alcohol a material containing 31.1 per cent of the dibasic acids is obtained. The dibasic acids probably occur in japan wax as mixed glycerides with oleic acid. The usual amount of dibasic acids in the wax is 5.2–6.3 per cent, but may be as high as 7.1 per cent.

The approximate composition of japan wax appears to be about as follows:

Glycerides of Monobasic Acids: 87 per cent
arachidin (1%)
palmitin (71%) [M. E. Tassily]
stearin
olein and linolein (11%)

Dibasic Acids (Japanic acids); combined as mixed glycerides with oleic acid: *5.2 to 7.1 per cent*

nonadecandioic acid	$(CH_2)_{17} \cdot (COOH)_2$
eicosandioic acid	$(CH_2)_{18} \cdot (COOH)_2$
japanic acid	$(CH_2)_{19} \cdot (COOH)_2$
docosandioic acid	$(CH_2)_{20} \cdot (COOH)_2$
tricosandioic acid	$(CH_2)_{21} \cdot (COOH)_2$(4–6%)

Free Monobasic Acids: 3 to 5 per cent
pelargonic
palmitic
oleic

Free Monohydric Alcohols: 1 to 2 per cent
pelargonyl m. 65° and (or)
arachidyl m. 66°
ceryl m. 79°
myricyl m. 88°

Sterols: less than 1 per cent
phytosterol m. 139°

Uses of Japan Wax. Japan wax, admixed with a considerable amount of paraffin, is used in the manufacture of candles, burnt in temples and houses in Japan. The wax is an aid in the vulcanization of rubber, but to no particular advantage over other fatty waxes. Because of its large saponifiable content it is of use in the manufacture of soaps, and glycerine may be obtained as a by-product. Japan wax is used in the manufacture of polishes, pomades, and in leather dressing. It is used by commercial laundries where it is worked in with starch to produce flexible starched fabrics. It is used as a sizing material or slip for cordage. For many purposes for which waxes in general are used japan wax is entirely unsuitable, because it is too fatty and too easily hydrolyzed. The available supply of japan wax has always been abundant, but the demand has greatly increased within recent years. The textile industries in the United States are at present very large users. Japan wax makes an excellent base for emulsifiable softening agents in finishing textiles.

About 3000 tons of japan wax are produced each year in China, and somewhat over twice that amount in Japan. Japan wax exported to the United States has been exported from Kobe.

Myrtle Wax

Myrtle wax is a wax derived from the fruit or berries of several species of *Myrica*, which genus belongs to the family order of *Myrtaceae* from which it derives its name. These are shrubs or small trees, about 35 species, 7 of which may be found in the United States; *Myrica carolinensis*, Miller, inhabits Canada to Florida along the Eastern coast. It is called the *wax-berry* or *bayberry*. The ripe drupes of the plant are separated, globose, bluish white in color, and very waxy. The plants grows in dry or moist sandy soil. It furnishes much of the bayberry wax of commerce. Another species is *Myrica cerifera*, L., which is a tall aromatic shrub growing in sandy swamps, or wet woods. Its leaves are serrated to some extent, differing from the unserrated leaves of M. carolinensis. This plant is found from New England to Louisiana. The common names for M. cerifera are wax myrtle, candle berry, candle-berry myrtle, wax berry, and tallow shrub.

The principal sources of myrtle wax are the United States, Colombia, Mexico, and South Africa. The Spanish name *arbol de la cera*, is generally applied to *M. jalapensis*, Kunth, of Mexico. The name *cape berry* is given to the shrub growing on the dunes in Cape Colony, South Africa, the species of myrtle being *Myrica quercifolia*, L., *M. cordifolia*, L., or *M. laciniata*, L.

The slender leaves of the myrtle are 2–2½ inches long and have resinous dots, on both sides, and are very fragrant when rubbed. The drupe grows in clusters of 1 to 1½ in. diameter, the berries being closely attached to the stem (in M. cerifera) and branches. The berries are gathered from the shrubs and boiled in water, and the wax melting and floating on the surface, is either skimmed off and strained, or allowed to concrete as the liquor cools, and then removed. It is then further purified by remelting and straining when it is cast into cakes. Much of the American myrtle wax, usually referred to as bayberry wax, is collected in the New England States.

A specimen of bayberries collected by the author along the sand dunes between Wildwood and Cape May, New Jersey, during the month of August yielded 7½ per cent of clean wax after boiling the berries in water for ten minutes. The wax is of a pale grayish green color, somewhat diaphanous, more brittle and unctuous to the touch than beeswax, of a pleasant odor, and of a slightly bitterish taste. The water in which the berries are boiled becomes wine-red in color and fragrant in odor. The wax had a density of 0.9538 at 15°, and 0.9775 at 25°. It melted at 44.8° (112.5° F) and the density of the melt was 0.8780 at 98°. It had an acid value 3.52, saponification value 208.0, and an iodine number (Hanus) 2.93.

Physical Constants of Myrtle Wax. Smith and Wade[128] had reported the following constants for myrtle wax: density 0.9806 at 22°/15.5°, 0.878 at 99°/15.5°, melting point 48°, solidifying point 45°, saponification value 217, iodine number (Hübl) 3.9, Reichert-Meissl number 0.5, acid value 30.7, and index of refraction n_D 1.4363 at 80°.

Somewhat different values have been reported by other investigators; density 0.99950 to 1.0262 at 15°/15°, 0.975 to 1.1098 at 25°/15°; melting point 40.5° to 48.0°, usually about 44.5°, solidifying point 39° to 45°, with mean at 42°. The melting point increases with the aging of the wax—and thus a fresh wax which melts at 48° in the course of four months might melt at 52.7°. The index of refraction is reported at 1.4360–1.4463 at 80°. Acid values have been reported from 2.5 to 21.2; the usual figure is not much over 4.0. The saponification value is quite constant ranging from 205 to 217, mean 213. The iodine number ranges from 1.03 to 3.9.

Arbol Wax. Mexican berries are reported to contain 7 to 12 per cent of greenish-white wax extractable by boiling water. The fruits are collected by Indians from the plants which occur in dense thickets covering considerable areas in Vera Cruz, and the wax is marketed in Mexico City. Arbol wax, as it is called, is more brittle and unctuous than beeswax, has a faint aromatic odor, a slightly bitter taste, and is not much lighter than water. It melts at 43°, but upon exposure the fusing point rises to 47.5°. A specimen from Tepic, Mexico, was greenish-white, another from Hildago greenish-yellow in color. The wax can be dispersed in 20 parts of hot water, but most of the wax deposits on cooling. It is soluble in most organic solvents and is easily saponified. Olsson-Seffer[108] has reported the following constants for Mexican myrtle wax: melting point 43.2°; density 0.8763/99°; acid value 4.2; saponification value 214.5; and iodine number 2.38.

Myrtle wax produced in Central and South America (probably from *M. arguta*, Kunth) is extracted from myrtle berries when they have matured to a light gray color, at which time the wax is most yellowish in color. The hard coating of wax is removed from the berry by boiling the berries in water and skimming the wax rising to the surface. The wax melts at 45°. The fatty acids solidify at 46.4°. Its acid value is 21.2, saponification value 216.7, iodine number 1.03, unsaponifiable 0.4 per cent, ash 0.06 per cent, and moisture 0.31 per cent.

Cape Berry Wax. Cape Berry Wax[134] is a wax derived from the berries of a species of myrtle, *Myrica quercifolia* (or, *M. xalapensis*, H.B.K.), growing in Cape Colony in South Africa. The wax is of grayish-green color, has a density of 0.874/99°; melts at 40.5°. It has an acid value of 2.5, saponification value 212, iodine number 2.0, unsaponifiable matter 2.5 per cent. Cape berry wax has also been termed South African berry wax. It is substantially the same as myrtle wax.

The South African Journal of Industry[116] describes a similar berry wax obtained from *Myrica cordifolia*, a bush growing on the sand drifts between

Port Elizabeth and Cape Town. An analysis gave the following values; melting point (of fatty acids) 47.5°; density 0.8741/99°, acid value 4.09; saponification value 211.0; iodine number 1.06; mean molecular weight of fatty acid, 236.1. Rindl[116] states that berry wax is obtained from different species of Myrica or myrtle, and gives the variations in five samples of the wax; melting point 40.5–45.0°; density 1.004–1.007 at 15°/15°; saponification value 211.0 to 214.6; iodine number 0–2.38, mean molecular weight of fatty acids 236.1.

Myrtle waxes are not true waxes, since in chemical composition they are largely triglycerides, and are readily saponified by alkalies. The glycerides are those of palmitic, and myristic acids, accompanied by a small amount of lauric, oleic, and stearic acids. The glyceryl ester *tripalmitin* is usually listed as the chief ingredient, although the chief fat of the Mexican berries appears to be trimyristin.

The wax in powdered form is a remedy for dysentery.[139] Mexican myrtle wax under the name of "arbol de la Cera" is used by the natives for treatment of diarrhoea and jaundice. Myrtle wax is sometimes used as a substitute for beeswax in the formation of plasters prepared by the apothecary. Its principal use in South Africa and in America is in the manufacture of very high grade candles and tapers. Highly decorative candles suited for Christmas and other festive occasions are made of myrtle wax. They are referred to as bayberry candles and they emit a fragrant odor when burning, although the light is less brilliant than that obtained from common lamp oil. Myrtle wax gives a splendid quality soap of white color, but the price is prohibitive for such use.

Wax of Mistletoe Berries

The white globose berries of the mistletoe *Viscum album*, L., have a deposit of wax in the cutinized layers of the epidermis, which causes water to flow over the cuticle without being absorbed. There is an appreciable amount of hydrocarbon in the chemical composition. From the petroleum ether extract of commercial bird-lime made from mistletoe berries the hydrocarbon, *triacontane*, m. 65°, has been isolated, and also *ceryl alcohol*. *Myricyl alcohol* and *urson*, m. 287°, have been isolated by other investigators. The ursolon is almost identical to the *ursolic acid*, m. 283°, of the cranberry. The wax also contains *stearic*, *palmitic*, *myristic*, and possibly *arachidic acids*. These acids are largely combined with the alcohols as wax esters.

The berries yield 5–6 per cent of extractives with petroleum ether, and the extractives contain a resin alcohol, *visciresinol*, $C_{16}H_{26}O_2$, and a wax alcohol, m. 71°, named *loranthyl alcohol*. The latter has the composition $C_{24}H_{50}O$, and is probably an isomer of lignoceryl alcohol.

It is interesting to note that bird-lime prepared from the drupes of the

European holly (*Ilex aquifolium*, L.) contains the sterol, α-amyrin, m. 181°. The latter exists as the ester, α-amyrin palmitate.

Cochin China Wax

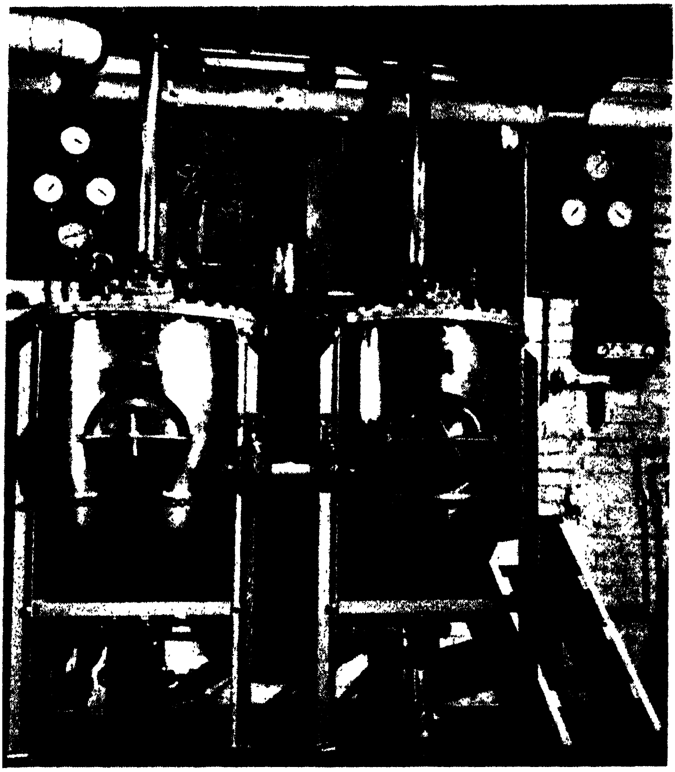
A product from the fruit of the cay cay tree growing in the far East is often listed under waxes, just as is myrtle wax, although both are very largely glycerides of myristic acid, and should be termed tallows. Cochin china wax has about the consistency of myrtle wax. The fruit of both *Irvingia Oliveri*, Pierre, and *I. malayana*, Oliver, the latter of Cambodia, yield the wax. The tree is a forest tree growing to a height of 100 feet, and belongs to the family *Simarubaceae.* The fruit is the size of a lemon, with a kernel the size and shape of an almond, and ripens in July when it falls to the ground. The natives gather them in heaps, where they are left for two months or until the soft outer parts decompose, when they are carried to the houses and spread out in the sun to dry. They are then opened by a strong knife, the kernels are removed, dried in the sun, and pounded in a mortar. The pulp is placed in sort of a crude double boiler, whereby a sticky paste is obtained which is wrapped in rice straw, and then submitted to pressure in a crude press, and the expressed wax is melted and cast into molds, or into candles in bamboo tubes provided with wicks. The dry kernels contain 52–60 per cent of wax, which is not fully recovered by the crude method of extraction. Press cake is used for fodder, fertilizer, or fuel. Five kilos of nuts yield one kilo of kernels and 430 grams of the fat or wax.

Cochin china wax is of a grayish color and may be refined by benzine extraction. The refined wax softens at 37°, melts at 39.7°, and solidifies at 31°. The wax has a specific gravity of 0.913 at 40°/40°. Its acid value is 0.86, saponification value 235.3, unsaponifiable 0.42 per cent, iodine number 6.7, Reichert-Meissl value 0.62. The insoluble fatty acids and unsaponifiable amount to 94 per cent, with melting point 38.8°, solidifying point 36.6°, neutral value 250.2, mean m. wt. 224. The native wax shows higher acid values, 23.5–34.9. Bontoux[17] gives the composition as *myristin* 60–65 per cent, *laurin* 30–35 per cent, and *olein* 5 per cent.

The native uses are as a candle making and soap-stock material. It is said to be similar to "dika butter" of West Africa and suited as an edible vegetable butter in chocolate making.

Cranberry Wax

Cranberry wax is the wax derived from the skins of the large or American cranberry, *Oxycoccus macrocarpus*, Aiton (*Vaccinum macrocarpon*, Ait.). It is natural to the outer skin of the berry where it serves as a water repellant. The wax coating is present to the extent of 0.15 of one per cent of the weight of the cranberry, together with a waxy water-insoluble substance known as *ursolic acid.* If petroleum ether is used as a solvent, in the cold, the wax may be extracted free from ursolic acid, but if dichloroethylene is used as the extracting solvent, ursolic acid is extracted as well as the wax. The wax cannot be appreciably removed from the skins by boiling water.

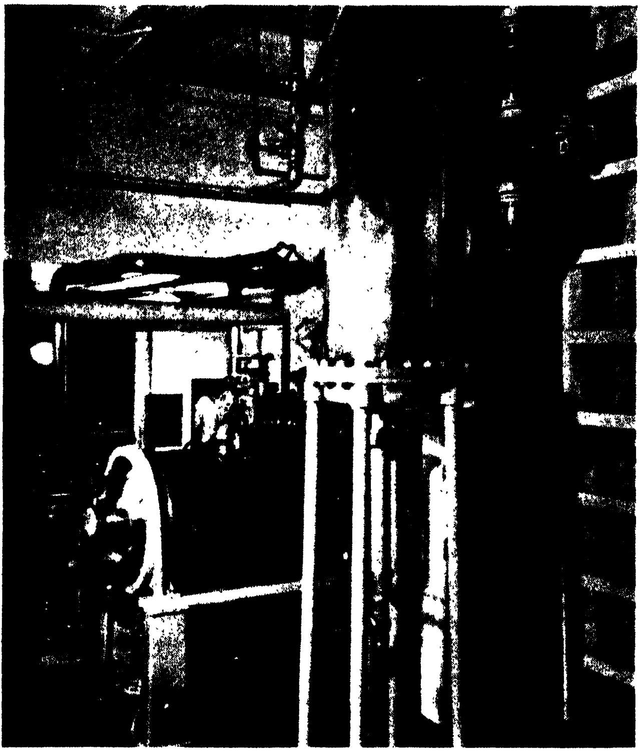


Courtesy Cranberry Packers, Inc., South Hanson, Mass.

FIGURE 9. Pilot plant for recovery of by-products of the cranberry.

Cranberry wax of commercial quality has been economically prepared from cranberry waste by Nealy, at the plant of the Cranberry Canners, Inc., South Hanson, Mass. The annual crop of cranberries is 500,000 to 800,000 barrels per year. From 1000 barrels of berries may be obtained about 2000 pounds of washed and dried pulp consisting of skins and 800 pounds of seeds. From the dried seeds mechanically separated from the pulp may be extracted 20–21 per cent of a greenish semi-drying oil, containing 200 units of vitamin A per gram; and from the dried skins about 12 per cent of a raw wax that the extractors refer to as *ursolene,* and which is marketable in the pulverized condition, and in addition about 10 per cent of crude ursolic acid.

Carleton, Morris and Nealy[25] describe the extraction process as follows: "twenty-five pounds of dried cranberry skins freed from seeds are placed in a copper cylinder (presumably a still with water cooled reflux condenser). Through this is passed the vapor of one of the extracting fluids for a period of time and at a definite temperature. It has been found that a 12 hour contact period is most effective for the extraction of either wax or acid from the skins. After one of the extracting solvents has been in contact with the skins for the desired length of time, the liquid flow is stopped and the second solvent permitted to contact the skins for an equal period of time. The action of the solvents is specific in that cold hexane will extract the *wax* from the skins but will only remove mere traces of the *uroslic acid.* Utilizing the same skins and treating them subsequently with dichloroethylene, practically all of the acid may be removed.



Courtesy Cranberry Packers, Inc., South Hanson, Mass.

FIGURE 10. Recovery of solvents in extraction of ursoline wax and ursolic acid from cranberry waste.

According to Nealy the character of the wax extracted from the skins is influenced by the temperature of operation of the still, and also the length of time of the extraction. After the extraction the solvent is recovered leaving the wax residue which can be separated as a layer. The product obtained from a low-temperature extraction with a considerable amount of water passing through the condenser is hence different from that of the high temperature extraction. The latter hexane extraction yields a residue which has a tendency to stratify into layers in which the *nonacosane* constituent separates. The name "Ursolene" is given to the product that represents everything extractable by hexane vapor at a temperature of 65–70° (146–158° F). As it comes from the still it is pulverized to make it uniform in quality. The still has a thermo-regulator control that makes it possible to lower the temperature of extraction by flowing more water through the condenser. By so doing most of the *nonacosane* is left behind and the product is dark colored. The wax is softer and of lower melting point, but can be hardened by a heat processing in which certain of the unsaturated fatty acid constituents apparently become oxidized.

Hence, several wax or waxy products can be commercially prepared, and these are summed up as follows:

(1) A soft greenish wax by using hexane as a solvent with low temperature on thermo-regulator. The wax has a melting point of approximately 74°, and is simply known as "cranberry skin wax."

(2) A hard, brownish wax by using hexane with a higher temperature. The wax contains a considerable amount of the hydrocarbon-nonacosane, which latter is only properly dispersed by pulverizing the wax product of the still. It has a melting point of 207.5 and is called *ursolene.*

(3) A paler gray-green hard wax, containing a considerable amount of nonacosane and of ursolic acid, by using dichloroethylene as a solvent. This wax has a melting point of about 217.5 and is known as "single extraction" wax.

(4) Heat processed cranberry skin wax in which an attempt has been made to oxidize the unsaturated fatty acids, and increase the melting point and hardness. The product is blackish.

(5) Ursolic acid, a white colored product, which is extracted from the *ursolene* residue after removal of the hexane extractable by dichloroethylene. This is "crude ursolic acid." The acid can be refined to obtain the c. p. ursolic acid, melting point 283° and neutralization value 122.8°.

In preparing "*ursolene*" the residue as removed from the still is first broken down into irregular lumps. It is seen to be non-homogeneous, and varies from gray to green in color. Upon further pulverizing it is of a greenish color. The so-called "single extraction wax" was first prepared by Nealy, and differs from the other waxes, in containing a larger proportion of ursolic acid plus much *nonacosane* with a lesser proportion of the softer wax constituents. It is hard and brittle. The constants for the cranberry wax and waxy products are listed in Table 14.

Table 14

	Cold Extraction Normal Hexane	Raw Cranberry Wax—Hot Hexane Extraction	Similar-Pulverized known as "Ursolene"	Single Extraction with Dichloroethylene	Hexane Extractive-Heat Processed with Blown Air	Ursolic Acid Purified
Melting point (°C)	74	212.0	207.5	217.5	194.0	283.0
Density 15°	0.970	0.975	0.975	0.970	1.010	0.970
Acid value	23.0	59.1	42.2	69.3	42.1	121.5
Saponification value	181.0	134.0	130	131	85.0	123.5
Ester value	158.0	74.9	87.8	61.7	42.1	2.0
Iodine number (Hanus)	69.0	52.2	53.2	44.2	57.4	55.7
Hardness 25° (Shore)	75	100	100	100	100	100
Ursolic acid (%) (estimated)	tr.	39.2	24.0	49.2	24.4	98.9
Hydrocarbons (%) (estimated)	7.2	15.9	23.5	13.8	23.9	none

Ursolic acid has an m. wt. of 456.68, a neutral value 122.8, and iodine number 55.6. The glycerides consist of about 20 per cent palmitin, 30 per cent of linolein plus linolenin, and 50 per cent olein, or their equivalents in mixed glycerides. The glycerides have a saponification value of 194, and an iodine number of 86. The free fatty acid is believed to consist principally of oleic acid, m. wt. 278.4, neutralization value 201.5, and iodine number 109.7. The free fatty acids constitute about 14 per cent of the proportional amount of the glycerides present in the wax. The composition of the cranberry waxes has been computed here on the basis of their chemical constants.

Approximate Composition of Cranberry Waxes

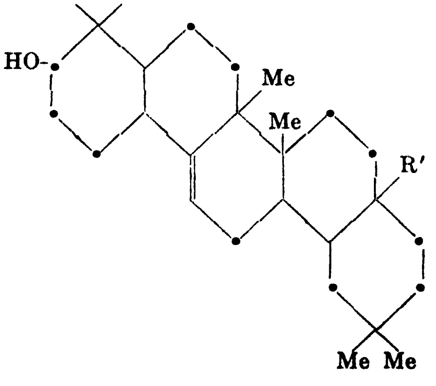
	Soft Wax m. 74° (cold petroleum ether extract) (%)	"Ursolene" m. 207.5° (hot normal hexane extract) (%)	"Single Extraction Wax" m. 217.3° (dichloroethylene) (%)
Mixed Glycerides of	81.4	46.2	32.5
linolenic acid			
linoleic acid			
oleic acid			
palmitic			
Free Acylic Acids	11.4	6.3	4.5
oleic acid			
arachidic (?)			
Free Polycylic Acids	mere trace	24.0	48.9
Hydrocarbons	7.2	23.5	14.1
nonacosane			
hentriacontane			

The heat processing of *ursolene* by blowing it with air causes a reduction in the glycerides content from approximately 46 to 23 per cent, but an increase in the free fatty acids from about 6 to 30 per cent, while the ursolic acid and hydrocarbons remain substantially unchanged.

The chemical composition of cranberry wax extracted from crude cranberry waste pulp by petroleum ether, has been given by Markley and Sando.[93] It was found to contain glycerides of linolenic, linoleic, and considerable oleic acid, besides a very large amount of unsaponifiable matter consisting of the hydrocarbons, nonacosane and hentriacontane. The solid fatty acids were of the usual mixture of plant acids of the series of C_{16} to C_{26}. In the distillation they separated seven fractions with 52.3° to 80.0° melting point, and the neutralization values ranged from 142 to 208. The four main fractions of hydrocarbons showed a melting point of 63.2–64.5°, and the chemical composition $C_{29}H_{60}$ and $C_{31}H_{64}$.

The cranberry dry pulp after extraction with hexane to recover the wax is treated with ethylene dichloride which extracts a waxy acid of considerable value, known as *ursolic acid.* Ursolic acid was first found in uva ursi leaves, but later in the skins of the apple, pear, and in considerable quantities in the skin of the cranberry. According to Nealy it is estimated that from twenty to thirty thousand pounds of ursolic acid a year can be recovered from cranberry waste now available for that purpose.

Refined ursolic acid is a very fine and fluffy white powder (231 cu in to 1 lb). It is refined through its monosodium salt from the impure form. It has no taste nor odor, is non-toxic, and is insoluble in water, hot or cold. It is soluble in alcohol, and in benzene. One per cent of ursolic acid in ammonia produced a thick colloidal solution. Chemically speaking, ursolic acid is a *sapogenin* with the formula $C_{29}H_{46}(OH)COOH$, and in the refined state as crystallized from 75 per cent alcohol, melts sharply at 283–283.2°, but it is not stable to heating at a high temperature. Methyl ursolate melts at 168–168.4°. Ursolic acid is a dihydric triterpene acid and its relation with allied compounds is shown in the structural formula of Huzii and Osumi[66] given below:



R′ = Methyl in α-amyrin R = methyl
R′ = CH_2OH in uvaol R = methyl
R′ = CO_2H in ursolic acid R = methyl
R′ = Methyl in β-boswellic acid R = COOH
Mark • denotes a CH_2 group

It will be noted that in ursolic acid there are 22 carbon atoms in rings and 7 carbons in the groups.

The ursolic acid in rhododendron leaves melts at 290–291° and is referred to as β-uroslic acid; the acid melting at about 285° as α-ursolic acid.

Ursolic acid according to Nealy[107] is an excellent emulsifying agent. It will produce what is known as a reverse emulsion, that is a water-in-oil emulsion instead of the usual oil-in-water type, the droplets of water being suspended in the oil instead of the oil in the water. As small an amount as three parts of ursolic acid to 1000 parts of the ingredients will produce a smooth, firm emulsion that will stand up without any support. It is said to be of value in preparing salad dressings.

A cream called Vaccinol has been prepared from cranberry seed oil, ursolic acid, and distilled water, which has proved valuable in the treatment of burns. It removes the soreness almost immediately and the burn heals in a very short time. Vaccinol has also been very successfully used in skin disorders such as eczema.

Apple Wax

The apple, *Malus malus*, L., and its many varieties, and related species contain a wax on the cuticle or skin. Sando[121] has reported on the wax obtained from the skins of Ben Davis, and Black Ben Davis varieties, and the numerous constituents that naturally occur in apple wax. One pound of wax is obtained from 43 square yards of skin from one type of apple to 231 square yards from another type of apple. 140–175 mg of wax can be obtained from 100 grams of "fresh tissue" by extraction with alcohol and ether.

In its crude state apple wax is a greenish yellow powder, resinous to the touch, and very repellant to water. It has a melting point of approximately 80°.

Apple wax was found to be chemically composed of *hexacosanol*, $C_{26}H_{53}OH$; *heptacosanol* $C_{27}H_{55}OH$, m. 81–81.5°; *octacosanol* $C_{28}H_{57}OH$; d-10 *nonacosanol*, $C_{29}H_{59}OH$; *triacontanol* $C_{30}H_{61}OH$; malol $C_{30}H_{48}O$, m. 284°–285°; *heptacosane* $C_{27}H_{56}$; *nonacosane* $C_{29}H_{58}$; and *triacontane* $C_{30}H_{62}$, m. 63.5–64°. *Malol* forms a crystalline monosodium salt and is dextrarotary. It has been found that malol contains a carboxyl group, and that it conforms to the generic formula $C_{29}H_{46}(OH)\cdot COOH$, comprising at least five condensed benzene rings and a number of methyl groups. Malol is now considered as identical to *α-ursolic acid* m. 285°, and consequently the name *malol* has been dropped. Ursolic acid in the purified state as crysstallized out from 75 per cent alcohol is a pure white crystalline powder, the crystals being prismatic in shape. Ursolic acid is insoluble in petroleum benzine, soluble in hot glacial acetic acid or alcohol; and moderately soluble in ether, acetone, and chloroform.

Pear Wax

A wax can be separated from the peels of pears, *Pyrus communis*, L., obtained in commercial canning according to Markley, Hendricks and Sando.[95] The wax is light green in color and of low melting point. The separation is effected with petroleum ether, and 40 per cent of the extract of the peels consists of free and combined acids, about half being in the unesterified state. The solid acids appear to be of the series C_{16} to C_{24}. The predominant acid is oleic, and very small amounts of linolenic and linoleic acids can be isolated from the liquid fraction. There is a small amount of glycerol but no secondary alcohols or ketones. The solid fraction contains the usual plant alcohols, ternary mixtures of the series C_{20} to C_{30}. *Nonacosane*, m. 65.1°, is the predominant hydrocarbon, and *ursolic acid* is a constituent. The latter had been previously extracted by Seifert in an impure form, m. 240°. The alcohol *10-nona-cosanol* had been definitely recognized.

Prunus Waxes

The wax in the skins of various species of *Prunus*, such as the cherry, *Prunus avium*, L., and the common prune, *Prunus domestica*, L., is much the same as in so many varieties of apples. The principal waxy constituent of the prune, previous to the researches of Van der Haar[54] in 1925, was called prunol, which proved to be the same as *ursolic acid* found in the skins of other fruits.

The skins of Bing cherries, *Prunus avium*, L., have been examined with respect to the constituents soluble in petroleum ether and ether, by Markley and Sando. From the petroleum ether extract there have been isolated or identified solid fatty acids consisting of a ternary mixture of *palmitic*, *stearic*, and a C_{18}-acid; liquid fatty acids, *linoleic* and *oleic*; a small amount of glycerol, and the hydrocarbons *nonacosane* and a higher one. The ether extract yielded a sterol and *ursolic acid.* The cherry yields 0.8 per cent of the dried skins in the wax constituents, and 0.1 per cent in crude ursolic acid.

Power and Moore[110] extracted 12.6 kilos of air-dried leave of *Prunus serotina*, Erhr., commonly called choke-cherry, with hot alcohol; the excess alcohol was removed by evaporation, and the resultant extractive was submitted to steam distillation. The distillate yielded a volatile oil, and the residue in the distillation flask consisted of a dark green aqueous liquid and a green resin. The latter green resin proved to consist of *hentriacontane* $C_{31}H_{64}$; *pentatriacontane*, $C_{35}H_{72}$; *ceryl alcohol, palmitic, stearic, linoleic* and *iso-linolenic* acids; *ipuranol* $C_{23}H_{38}O_2(OH)_2$; *prunol* (ursolic acid), m. 275–276°.

Grape Pomace Wax

In 1938 Markley, Sando, and Hendricks[94] reported on the air-dried pomace from Concord grapes, *Vitis labrusca*, L., which they exhaustively extracted with petroleum ether and ether, to obtain respectively 4.0 and 3.4 per cent of extractives. The saponifiable of the petroleum ether extractive revealed glycerol; linoleic, oleic, palmitic, and stearic acids, and higher saturated acids of the series C_{20} to C_{32}; the hydrocarbons, *nonacosane*, and *hentriacontane*; *sitosterol*, and fractions representing mixtures of primary alcohols of the series C_{22} to C_{28}. The ether extract consisted principally of *oleanolic acid* $C_{30}H_{48}O_3$, together with unidentified resinous substances. Like the *ursolic acid* found in the skin of the cranberry, oleanolic acid is a sapogenin aromatic polyterpene like bodies of vegetable origin containing a nucleus of probably five condensed benzene rings. Oleanolic acid is also found in the sugar beet, on the clove bud, and in olive leaves.

The most valued constituents of the waxes on the various fruit skins are the *sapogenins*, which can be freed from the saponifiable matter with treatment with dilute caustic soda, acidifying and crystallizing the sapogenin from a 75 per cent alcohol solution. The sapogenins are valuable as emulsifying agents. They are not toxic and can be used for coating any delicate object that needs to be moisture proofed, such as nuts, cookies, candies, etc. They will probably prove to be of considerable value to the cosmetic industry as well.

Cocos Wax

Cocos wax is a wax derived from the fruit of the *Cocos nucifera*, L., the coco palm found in all tropical countries. It is found as a residue in the storage tank sediment of coconut oil from which it can be refined. Cocos wax has a melting point of 80–85°. It should not be confused with *coconut stearine*, which is a fat, or with cocoa butter (m. 21.5–27.8°) which is purely a fat derived from the seeds of *Theobroma cacao*, L., growing from Brazil to Mexico.

Raspberry Oil Wax

A wax of exceedingly limited amount, but at least of academic interest, is the wax extracted from raspberry oil. This appears to have been first separated from raspberry oil by Marcelet,[91a] and consists very largely of the 22.8 per cent of unsaponifiable constituent of the oil itself. From the unsaponifiable matter Marcelet isolated the alcohol $C_{19}H_{40}O$, m. 62.5°, which corresponds to *nonadecyl alcohol*, m. 63°.

Ucuhuba Wax

Ucuhuba wax is a wax derived from the kernels of the fruit of *Myristica surinamensis*, Roland, an aromatic tree, growing in Brazil. The wax may be extracted from the seed with a suitable solvent, or by melting it out with boiling water. The wax is also called ukahuba, or ocuhuba, fat, and should be properly classed as a vegetable tallow. The genus *Myristica* includes *M. argentea*, source of the Papua and Macassar nutmegs; *M. bicuhyba* of Brazil whose black wrinkled seeds are the source of a vegetable tallow; *M. fragrans* of Molucca Islands which is the source of U.S.P. nutmegs, nutmeg butter, and mace; also many allied species: *M. otoba* of northwestern South America whose seeds are a source of Otoba butter, the arilloid of the fruit being white mace. The word "myristica" is derived from the Greek "fit for anointing."

Ucuhuba wax has a melting point of 39–45°, a specific gravity of 0.995 at 15°, 0.8855 at the melting point, and refractive index n_{10} 50.1–61.6. It has a minimum acid value 20.7, saponification value 215.1 to 229.0, iodine number (Wijs) 10.9–14.1; Hehner number 93.4, and unsaponifiable 0.1 to 3.9 per cent.

The chemical composition of the fatty acids derived from the seed wax or fat have been reported as lauric 5.0–13.3, myristic 66.6–73.0, palmitic 8.9–11.0, oleic 6.6–11.0, and linoleic 3.0 per cent. The seeds yield 64–70 per cent wax or fat, which consists principally of *myristin*, about 10 per cent *olein* and 7.7 per cent resinous matter which is insoluble in petroleum ether, and gives a fuchsin-red coloration on the addition of a drop of concentrated H_2SO_4. The resin melts above 100, has an acid value of 105.5, saponification value 195.3, and unsaponifiable 3.9 per cent. The brown color of ucuhuba wax or fat has interferred with its use commercially. The resinous portion is believed to be somewhat toxic.

Closely related is ocuba wax, derived from the seeds of the fruit of a tree, *Virola sebifera*, Aubl., sometimes classified as *M. virola* or *M. ocuba*. Its habitat is Brazil, Guiana, and Panama. It is also called virola tallow. It consists of a yellowish tallow-like mass, has a slight ethereal odor, melts at 40°, and has a specific gravity of 0.920 at 15°. It is used by natives in making candles, and ointments.

Gueriniella Wax

A wax derived from a plant, *Gueriniella serratula*, Fabricius, has been studied for its chemical and physical constants by Prandi. The crude wax is reddish-yellow in color and of a disagreeable rancid odor, and was found to contain 23.8 per cent of ether-soluble fatty substances. This mass had a melting point of 54–56°, setting point 49–51°, density 15°/15°

0.874, and contained 26.5 per cent free fatty acid. The ether-insoluble waxy substance recrystallized from benzene formed minute white scales of silky luster and unctuous feel. The constants for the wax are as follows: melting point 88–89°, solidifying point 88°, density 15°/15° 0.985, refractometric degree (Zeiss butyro-refractometer) reduced to 40°, 48.7; saponification value 69; acid value 0; ester value 69; Hehner number 53.3. The wax is very soluble in hot benzene, chloroform, and carbon disulfide; quite soluble in cold chloroform and in carbon disulfide; and slightly soluble in cold benzene. It contains no unsaturated compounds and no cholesterol.

It is formed chiefly of *myricyl myricinate* and small amounts of esters of ceryl alcohol and unidentified acids. It is probable that the ester in its purified state would have a melting point of 90.5°.

Opium Wax

Opium wax is a constituent of the concrete exudation from unripe capsules derived from *Papaver somniferum*, L., indigenous to the Mediterranean region, and cultivated in India, and commonly known as opium poppy, cheesebowl, pushbole, or marble flower. The wax is contained in the pericarp of the seeds.

About seven per cent of a brown sticky wax can be extracted from dry powdered opium by means of petroleum ether. The wax is insoluble in water, almost insoluble in alcohols, and soluble with difficulty in acetone; but freely soluble in chloroform, carbon tetrachloride, ether, benzene, etc. It contains 28.7 per cent of unsaponifiable matter (iodine number 138.5). The wax shows a very high iodine number 152.5; a Reichert number of 2; and saponification value of 114.5. One of the known constituents of opium wax is ceryl palmitate.

Wax From Rice Polishings

The polishings of rice, *Oryza sativa*, L., yield a wax which consists largely of a wax ester of high molecular weight. To prepare the ester the rice polishings are extracted with hot 90 per cent alcohol. On subsequent cooling a precipitate results which has proved to consist principally of melissyl cerotate, $C_{26}H_{53}CO \cdot O \cdot C_{31}H_{63}$. The wax melts at about 85°.

Waxes in Citrus Peels

The rinds of the sweet orange, *Citrus aurantium*, L.; bergamot orange, *C. bergamia*, Risso, source of the oil of bergamot; lemon, *C. limonum*, Risso; bitter orange, *C. vulgaris*, Risso, the flowers of which are the source of the oil of Neroli; and the lime, *C. limetta*, Risso; and grapefruit, *C. grandis*, all yield very small amounts of wax. The citrus waxes are soft and of relatively low melting points. They are extractable from the dried fruit rinds by treatment with chloroform. Some of the wax constituents may be found in the pulp as well as in the peel.

Citrus aurantium sinensis, L., the Valencia orange, contains wax acids, believed to be *lignoceric* and *cerotic* (*b*) acids. The straight chain C_{26} acid has been established with certainty. The wax also contains esters of a phytosterol, probably *sitosterol*. Fatty constituents such as oleic, linoleic, palmitic and stearic acids have been found, and are common to other citrus fruit peels. The pulp contained the hydrocarbon, pentacosane, which is not present in the peel. The peel contains higher hydrocarbons.

The non-volatile waxy residue remaining after distillation of Florida grapefruit peels contains, according to Markley,[96] solid waxy acids of the mean molecular weight $C_{32}H_{64}O$; *linolenic, linoleic,* and *oleic acids*; a sapogenic ketone, $C_{30}H_{52}CO$; hydrocarbons $C_{29}H_{60}$, *nonacosane*, and $C_{31}H_{64}$, *hentriacontane*; a *phytosterol*, $C_{25}H_{47}OH$; and *umbelliferone*, $C_9H_6O_3$. These substances have their origin in the cuticle wax of the fruit which wax is dissolved by the oil during the pressing process.

WAXES IN SEEDS

Sunflower Seed Wax

Sunflower seed wax is found in the hulls of the seed of *Helianthus annus*, L. This wax was discovered in a peculiar way and reported by Barenther[11a] in Germany in 1923. He stated, "An isolated tank of sunflower oil, from the center of which oil was withdrawn while fresh oil (10 carloads) was pumped in on top, showed at the end of the season that the oil at the bottom became turbid and gelatinous at 30°. A careful separation and analysis of the turbidity proved it to be *ceryl cerotate* wax, to the amount of 0.14 per cent on the basis of the residual oil left in the tank, and its source was traced to the hulls of the sunflower seed, found to contain 10 per cent of this wax. It is concluded that the wax separated from the oil during cold weather." *Ceryl cerotate* has the formula $C_{52}H_{104}O_2$, and melts at 84°.

Afridi Wax

Afridi wax is the wax produced by boiling safflower oil, obtained by a hot pressing of the seeds of the safflower, *Carthamus tinctorius*, L., a plant cultivated in India for the preparation of the saffron dye. The oil contains a considerable amount of unsaturated acids and is a drying oil. Natives heat the oil when using it for the preservation of leather vessels, ropes, etc. By boiling the oil in earthenware vessels, and immediately placing it in flat dishes partly filled with cold water, it solidifies to a thick jelly-like mass termed "roghan," or the boiled oil is, according to Lewkowitsch, employed by the natives of Lahore, Delhi, Bombay, and Calcutta for the manufacture of "Afridi wax linoleum." Roghan is also used by the natives for drawing artistic designs on woven cloth. The application to the drawn design is by finely pointed staves dipped in the "roghan" which is drawn out in very fine threads, and so deposited on the cloth. When completely dry, it forms an indelible pattern.

Corn Wax

Corn wax is obtainable in small quantities from the sludge that settles out in chilling crude corn oil from Indian corn, *Zea mays*, L., by separating it, treating it with an equal volume of ligroin to dissolve out the residual oil, and then centrifuging out the waxy mass. Shriner *et al.*[126] dissolved this waxy mass, or thick semi-solid paste, in hot ligroin, filtered the solution and allowed it to cool. About 220 grams of solid matter were obtained from 13.5 kilos of the original sludge. This material still contained some oil and was recrystallized from amyl alcohol, boiled with acetone, in which the wax is insoluble when cold, filtered and then finally recrystallized from ligroin, from which it separated in feathery crystals, m. 81–82.5°. The yield was 120 grams. These crystals had a molecular weight of 778.8. The calculated molecular weight for a myricyl ester of docosanoic acid is 760.4, of tricosanoic acid 774.4, and of tetracosanoic acid 788.4.

The wax is insoluble in cold ether, alcohol, ligroin, amyl alcohol or benzene but it is somewhat soluble in carbon tetrachloride and chloroform. A chloroform solution of the wax was optically active. The wax purified as described was saponified by refluxing with alcoholic potassium hydroxide for 48 hours. Warm water was added and the hot solution was extracted with successive portions of hot benzene. Upon the evaporation of the benzene the myricyl alcohol separated out with melting point of 82–84°. It was again boiled with alcoholic KOH, an alcoholic solution of calcium chloride added to precipitate traces of fatty acids, and the hot solution, after it had been filtered, was diluted with water and the *myricyl alcohol* filtered off. The substance was then recrystallized from alcohol and benzene (1 : 1) and from ligroin, after which it melted at 87–88°.

The myricyl alcohol obtained from corn wax was found identical to the myricyl alcohol prepared from beeswax, and a mixed melting point with that obtained from corn wax showed no depression. Shriner pointed out that the melting point of myricyl alcohol is often given in the literature as 85°. In order to raise its melting point to 87–88° it is necessary to treat it with alcoholic KOH twice and then recrystallize from a mixture of benzene and alcohol (1 : 1) and from ligroin.

The fatty acids in corn wax were separated by acidifying the soap solution, freed from the myricyl alcohol, with hydrochloric acid, and removed as a cake after the mixture had cooled. It was then recrystallized from alcohol and acetone, after which the acid melted at 74° and had a neutral equivalent of 357. The acid was esterified by refluxing with methanol and concentrated sulfuric acid. The ester formed an oily layer and when chilled was separated, dried and distilled. The acids were then isolated from their methyl esters. Both *n-tetracosanic acid* and *iso-behenic acid* were positively identified. Hence the solid matter separated as a wax from corn oil consists largely of the *myricyl esters* of *tetracosanic* and *iso-behenic acids.* The presence of *hentriacontane, sitosterol* and *stigmasterol* have been reported.

Koryan (Kaoliang) oil is pressed from Koryan corn of Manchukuo, the yield being 3.3 per cent. This oil contains 7.6–8.6 per cent of unsaponifiable matter which when extracted with ether gives 2 per cent of *takakibyl alcohol* $C_{44}H_{89}OH$; 12 per cent *koryanyl* alcohol $C_{28}H_{57}OH$; 21.6 per cent sitosterol; and 63 per cent of a mixture of *cetyl* alcohol and an alcohol $C_{30}H_{48}O$. The extract with benzene yields 6 per cent takakibyl alcohol; 28 per cent koranyl alcohol and 50 per cent of sitosterol, cetyl alcohol, etc.

In the pollen of Japanese white flint corn, *Zea indurata,* there is a waxy material which consists largely of *phytosterol palmitate* m. 88–88.5°, which Anderson[2] hydrolyzed into *palmitic acid* m. 62.5°, and two *phytosterol* fractions m. 122° and 136.5°. Anderson also found *n-nonacosane* $C_{29}H_{60}$, an unidentified alcohol $C_{30}H_{61}OH$ m. 136°, and a phosphatide containing 4.09 per cent phosphorus.

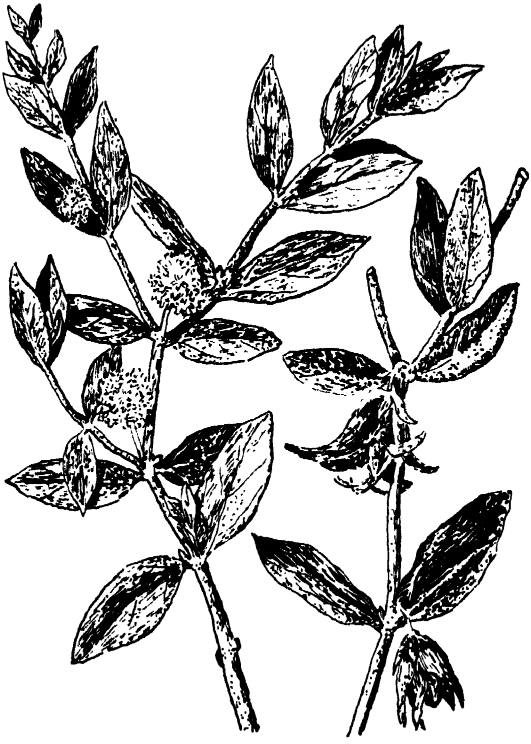
Anderson later found that the endosperm of corn contains some free *phytosterol,* m. 137–137.5°, and rather large quantities of ordinary *sitosterol,* and the optically active *dihydrositosterol,* $C_{27}H_{47}OH \cdot H_2O$, m. 140–141°.

Jojoba Wax

Jojoba wax, or jojoba (pronounced hohóba) oil, is derived from the coffee-bean-like seeds of the jojoba, *Simmondsia californica,* Nutt., of the family Buxaceae, an evergreen shrub growing in great abundance on rocky hillsides in Arizona, California, and Western Mexico. The seeds on pressing yield an oil which in some respects is not unlike sperm oil. The peculiar composition of jojoba oil places it in a category of liquid waxes, since it is composed almost entirely of high molecular weight, monoethylenic acids and alcohols. That the oil is a liquid wax was first discovered in 1933 by Greene and Foster.

According to Markwood[96a] the seed of jojoba, or goat nuts, as they are frequently called, contain more than 50 per cent oil. Ordinary cottonseed crushing equipment serves to expel the oil. On a small scale it is more convenient to operate by solvent extraction, preferably using light petroleum, extracting the nuts after they have been ground. The solvent is then distilled off, and a residual oil of a slightly yellowish color is left. Most of the color can be dispelled by heating the oil for a short time to about 288° (550° F). The nuts are one-half inch long and three-eighths of an inch across and 35 nuts make up an ounce. The nuts can be collected by hand labor, and quantities have been shipped to Europe from Mexico, attesting to the feasibility of handling on a commercial scale.

McKinney and Jamieson[101] report the following constants on oil from Mexican seed: $n_{25°}$ 1.4648, density$_{25°}$ 0.8642, iodine number (Hanus) 81.7, saponification value 92.2, acid value 0.32, unsaponifiable 48.3 per cent, saturated acids 1.64 per cent, iodine number—total fat acids 76.1, neutral value of total fat acids 172.0, and glycerol none.



After A. E. Hoyle

FIGURE 11. Flowering shrub and fruit of *Simmondsia californica*, Nuttall.

Composition of Jojoba Oil. McKinney and Jamieson[101] obtained 3 liters of a light yellow limpid oil by grinding twenty-five pounds of seed from the State of Sonora, Mexico, in a Hobart mill, and then extracting by cold percolation with petrolic ether, followed by removal of solvent by distillation and careful evaporation. The acetyl and iodine numbers of the unsaponifiable matter indicated that it consisted very largely of unsaturated alcohols, and they found no saturated alcohols or hydrocarbons. The unsaponifiable matter was completely hydrogenated by Adams platinum catalyst, and then by oxidation with chromium trioxide in glacial acetic acid, conversion by calcium to calcium salts, and hydrochloric acid decomposition of the latter, the fatty acids were recovered and purified by crystallization from alcohol. The fatty acids melted at 68.4–69.0°. The mean molecular weight of 335, based on the neutralization value of 167.5, indicated behenic acid, thus establishing *docosenol* as the chief alcohol constituent of the unsaponifiable matter.

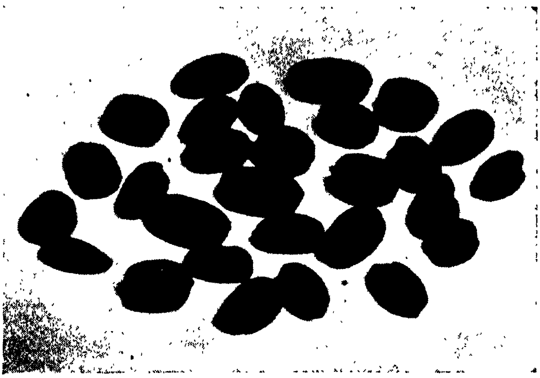


FIGURE 11a. Coffee-bean-like seeds of the jojoba have a thin, dark-brown pericarp which covers a white perisperm rich in liquid wax.

FIGURE 11b. Highly lustrous, pearly white, crystalline laminae of hydrogenated liquid wax. The solid wax melts at 70° (158° F).

A 100-gram portion of the original oil was saponified, the acids converted into their calcium salts, and the fatty acids liberated therefrom by hydrochloric acid, and then taken up with ether. The major portion of the unsaponifiable matter separated as an upper liquid phase, from which later on 10.3 grams of higher fatty acids were obtained. Upon evaporation of the ether 43.2 grams of acids were obtained. These acids were converted to potassium salts, then to ethyl esters, which were fractionally distilled under reduced pressure from a Ladenburg flask. Four fractions, I, II, III and IV were obtained. The first fraction was redistilled to yield other fractions. Fraction I_a was hydrogenated and from this fraction was recovered pure eicosanic acid, and small amounts of stearic and palmitic acids, originating from the *eicosenoic, oleic* and *palmitoleic acids* in the oil.

About two grams of the esters of fraction II were hydrogenated, saponified, and the fatty acids liberated and crystallized from alcohol. The first crop of crystals were identified as eicosanic acid contaminated with a little behenic acid. Fraction IV also proved to be a mixture of eicosanic acid and behenic acids, the behenic acid being the principal constituent. Fraction III was similar.

The second portion of fatty acids (10.3 grams) separated from the unsaponifiable matter was converted into their crystal esters in the usual manner and the resultant esters were distilled under diminished pressure from a small Claisen flask equipped with a fractionating column. An examination of the saponified products revealed about one-third of unsaponifiable. The latter was separated and after hydrogenation crops of crystals containing 50 : 50 molar mixtures of eicosanic and behenic acids were obtained. These acids had a mean molecular weight of 326, and a melting point of 70.8.

The unsaponifiable fraction (49.6 grams) separated from the 100-gram portion of jojoba oil was refluxed for several hours with a large excess of acetic anhydride. The unreacted acetic anhydride was decomposed with water, and the separated alcoholic acetates were washed free of acetic acid. The dried acetates (51.9 grams) were distilled to give fractions I to IX plus residue (X). From the iodine numbers, refractive indices, and the acetyl values, and melting points of the hydrogenated acetates, the presence of *eicosenol, docosenol,* and *hexacosenol* was definitely established as the alcohol components of jojoba oil. Hexacosenol is the only unsaturated alcohol that is solid at room temperature.

The percentage chemical composition is reported as saturated acids 1.64, *palmitoleic acid* 0.24, *oleic acid* 0.66, *eicosenoic acid* 30.3, *docosenoic acid* (erucic) 14.2, *eicosenol* 14.6, *docosenol* 33.7, and *hexacosenol* 2.0. Green, Hilditch, and Stainsby[51] state that the chief acid is $\Delta^{11,12}$-eicosenoic acid; $\Delta^{13,14}$-docosenol, and $\Delta^{11,12}$-eicosenol have been identified as the alcohols; 11,12-*dihydroxy-eicosanoic acid* m. 130.5° is also identified.

Jojoba oil is said to have been used by the Indians as a hair dressing. The Northwestern University Medical School has been reported as working on the liquid wax of the jojoba bean as a carrier for medicinals injected by needle. Markwood first noted the stability of the oil to heat, and states that the oil can be repeatedly heated to 550° F without any apparent decomposition, thus making it suited as the fluid medium for an instrument such as a melting-point apparatus, and that it is superior to various organic synthetics for that purpose. Jojoba oil is excellent for liquid heat transfer, particularly where heat must be carefully controlled. It is valuable for lubricating purposes, and may be used for delicate mechanisms. It is likely to prove of considerable value in the field of cosmetics, and in typing ribbon inks, etc.

Celery Seed Wax

The seed of *Apium graveolens*, L., contains a very small amount of wax. This wax can be recovered from the sludge which settles out from the commercially extracted celery seed oil, prepared by the alcoholic extraction of ground celery seed originating from France or India. When the ground seed is extracted with warm alcohol, and the alcohol is boiled off, there is left a thin, green oil of strong celery odor. Upon standing several hours a sludge settles out from which the thin oil is freed. Currier observed that the sludge contained a considerable proportion of waxy matter. Celery seed oil has a congealing point of − 12°, an acid value of 2, a saponification value of 178, iodine number (Wijs) of 108, and a mean molecular weight of 317 for its fatty acids, which comprise 93 per cent of the weight of the oil. The fatty acids have a neutralization value of 177.2 and iodine number of 93.4. The oil apparently consists largely of the following triglycerides: *olein*, *linolin*, *linolenin*, *gadolein*, and *erucin*.

The sludge from Indian seed was extracted with benzol, followed by carbon tetrachloride. Either one of these solvents will remove much of the oil, but the best solvent for removing the oil from the sludge proved to be acetone, which leaves the waxy material in a semi-refined state if the acetone extract is decanted in the cold and the residue carefully washed with fresh acetone, and dried.

The semi-refined wax which represented 89.6 per cent of the weight of the sludge gave the following constants: melting point 99.4°; saponification value 211.3; acid value 25.6; iodine number 47.3. The wax is partially soluble in water, soluble in very dilute nitric acid, partially soluble in ethanol; and insoluble in carbon tetrachloride. That portion which is soluble in water is bleachable to a pale color with charcoal, and has somewhat of a gel consistency and is of pleasing odor. The insoluble portion is dark in color and quite hard. The wax apparently contains a proportion of dibasic acids existing in part as glycerides, also hydroxy lactones, and mono-ethanoid alcohols.[148]

Soya Bean Wax

Soya bean wax, or soybean wax, is derived from the seed of *Soja hispida*, Moench, called in Japan "miso", and can be obtained from the press cake by extraction with suitable solvents. Wax from the winterizing of soybean oil contains approximately 10 per cent of free alcohols, ranging from C_{32} to below C_{28}, while the acids in the form of alkyl esters have an average chain length of 22 carbon atoms. No free acids or hydrocarbons are present. The presence of two phytosterols is indicated. The wax amounts to about 0.002 per cent of the original oil.

In the high-pressure hydrogenation of soybean oil Shinosaki and Kubo[125] found that at 350° an almost entirely wax-like substance was formed. The chemical characteristics of the ester formation appear to be a function of the reaction temperature. At temperatures above 300°, decomposition of soybean oil glyceride and alcohol formation occurs, and above 350° unsaponifiable matter, probably hydrocarbons, (including *octadecane*) are produced. The esterified wax substance is comprised largely of an ester of *stearic acid* and *octadecyl alcohol*, which ester has the following constants: melting point 58.5°; saponification value 102.4; acetyl number 0.9; iodine number 0.4; density 65°/4° 0.8296; refractive index $n_{65/D}$ 1.4419. The catalyst used in the hydrogenation was copper carbonate on infusorial earth, and the pressure 125 kg/sq cm in the autoclave.

Sesame Seed Oil Wax

A wax has been reported as constituting the chief component of a sludge of the "black" seed oil derived from *Sesamum indicum*, L., a species of herb growing in Africa. The waxy matter is responsible for the cloudiness that develops in oil that has been doubly refined, in the course of a few days. The saturated wax has a melting point of 80°, and is optically active. It is insoluble in ethyl ether, soluble in hot absolute ethanol, and in hot benzol. The waxy substance contains no nitrogen, sulfur, halogen compounds, sterols, glucosides or carbohydrates.

Coffee Berry Wax

There is very little wax in the coffee berry, but an appreciable amount can be recovered as a by-product when the coffee bean is extracted in large quantities in the Kaffee-Hag process. Coffee berry wax may be defined as the wax of the seeds of *Coffea arabica*, L.

Coffee berry wax is dark grey in color and of a firm but semi-hard consistency. The crude material has been referred to as fat of the coffee seed, particularly since it contains a relatively large amount of fat acids, such as oleic and palmitic, with some myristic and stearic acids, and traces of arachidic acid.

It has been reported that the crude wax contains as much as 26–62 per cent of *linoleic*, and 17–31 per cent of *oleic acid*. In 1911 Meyer and

Eckert[102] reported that the fat of the coffee bean contained 21.0 per cent of unsaponifiable wax, which gave a phytostearin reaction, and that it seemed to comprise *tannol carnaubate.*

Wagner[144] found the coffee berry wax to yield 1.64 per cent of ash consisting mostly of FeO and SiO_2. Phytosterol is an oxidation product of kahweol, both being constituents of the wax. The unsaponifiable soluble in petroleum ether not only contains phytols, but a fatty acid of 362.4 molecular weight, which melts at 84.6°. This acid might prove later to be *lignoceric* with a trace of *hexacosic acid.* Phosphatides have also been identified.

In view of the work of Meyer and Eckert[102] and more recently that of Wagner[144] and others, the chemical composition of the unrefined or semi-crude wax is beginning to become known.

Approximate Composition of Crude Coffee Berry Wax

Tannol Ester of Monbasic Fatty Acid: 21 per cent
tannol canaubate

Glycerides of Saturated Monobasic Fatty Acids: 50–52 per cent
palmitin, $C_3H_7(C_{16}H_{33}O_2)_3$ (12½–14%)
behenin, $C_3H_7(C_{22}H_{43}O_2)_3$ (1%)
lignocerin, $C_3H_7(C_{24}H_{47}O_2)_3$ (36–37%)

Glycerides of Unsaturated Monobasic Fatty Acids: 18–19 per cent
linolein, $C_3H_7(C_{18}H_{33}O_2)_3$ (8–9%)
olein, $C_3H_7(C_{18}H_{35}O)_3$ (10%)

Free Fatty Acids: 1 per cent
palmitic
behenic

Sterols: 2–3 per cent
phytosterol, m. 138.4°
kahweol, m. 143.5°
cafesterol, m. 156°

WAXES FROM FLOWERS

Many of the flowers yield small amounts of waxes, which are obtained as a by-product of their essence; they are residues which are insoluble in cold alcohol. These floral waxes are not usually obtainable in quantity sufficient to be of any extensive commercial value. They are of scientific interest because of their peculiar composition, and there is not a great deal known about them. The flower waxes are generally obtained in a semi-crude state and amongst them may be mentioned mimosa wax, *Leucaena glauca,* Bentham, which is reddish-brown in color; lavender wax, *Lavandula vera,* L., buff in color; jasmine wax, *Jasminum grandiflorum,* L., brownish-red in color; and rose wax, *Rosa centifolia,* L., olive-green in color.

All of the floral waxes are quite plastic in character, and bear some resemblance to beeswax. Their plasticity has been ascribed to the presence of metasterols and certain aromatic alcohols. The hydrocarbons and some of the higher wax alcohols and esters comprise the higher melting and harder constituents. Since floral waxes contain from 0.8 to 4 per cent of essence, they are of value as perfuming agents in the milling of sweet-scented soaps.

The floral waxes are characterized by their high hydrocarbon content, namely 30 to 60 per cent, contrasted with beeswax which has only 12 per cent of hydrocarbons.

Rose Wax

Rose wax is obtainable as a residue in the solvent extraction of the essence from *Rosa spp.* According to Prophéte[111] the wax melts at 61°. It is completely soluble in chloroform, benzene, carbon disulfide, and petroleum ether; and is partially soluble in alcohol, ether and acetone. The following chemical constants have been determined: saponification value 29.8; acid value 3.15; ester value 26.55; iodine number 13.0; Reichert-Meissl value 1.35; Hehner number 97.4; acetyl value 31.

Rose wax, according to Prophéte,[111] has the following chemical composition:

	Per Cent
Water	0.68
Acids: soluble (1.6%) insoluble saturated (10.6%) unsaturated (6.4%)	18.70
Unsaponifiable: hydrocarbons (51.5%) alcohols (20.2%) hydroxy acids (3.2%)	80.20

The alcohols *pseudocerylic* (3 per cent) and *isocerylic* (6 per cent) are present in combination with the fatty acids as esters. Other alcohols found were $C_6H_{12}O$ (8 per cent), $C_{10}H_{20}O$, m. 49.5° (1.5 per cent), $C_{10}H_{20}O$, m. 43.0° (1.0 per cent), and an alcohol m. 16.0° (0.5 per cent). The $C_{20}H_{10}O$ alcohols are of the olefinic terpene type (*e.g.* rhodinol). The saturated hydrocarbons identified were of 18, 20, 21, 22, 23, 26, 27, and 30 carbon atoms. The hydrocarbon $C_{27}H_{56}$ was present to the extent of 15 per cent of the total wax. The terpene alcohols have an esterogenic action.

Louveau in 1931 reported constants for the rose wax of the Provence rose, *Rosa centifolia*, L., which are at variance with those of Prophéte in the acid and ester values, but in fair agreement in melting point and in hydrocarbon content. Louveau's constants are: density$_{15°}$ 0.970–0.988; melting point 59–60°; acid value 38.5–39.4; ester value 80.8–86.7; hydrocarbons 50–52 per cent.

D'Ambrosio[32a] who in 1926 had examined the wax of the Druscky rose found an unsaturated acid, identified as *oleic acid,* also a hydroxy acid, identified as *9-hydroxystearic acid.* The crude wax was an intensely yellow amorphous mass, m. 57–58°, the surface of which was covered with rhombic crystals. The wax is partially soluble in hot alcohol. From the alcohol soluble portion a white wax m. 71–72° could be only incompletely crystallized from a benzene-petroleum ether (1:3) in acicular form. From the crystal wax he isolated an acid $C_{18}H_{36}O_3$, m. 73°, which was named *rosilic acid.* Rosilic acid he believed to be identical to *9-hydroxystearic acid.* From the mother liquor was isolated an acid, m. 70°, acid number 3.9. This on saponification gave rosilic acid, and proved to be an *etholide* of 5 carboxyls. A dihydroxy acid was isolated and identified as 9, *10-dihydroxystearic acid,* m. 137°. There was also present a compound composed of acicular crystals, m. 119° which could not be identified. It is insoluble in acetone. A secondary alcohol, $C_{17}H_{36}O$, m. 60–61°, was identified as $Me(CH_2)_7CH(OH)(CH_2)_7Me$.

Wax From Violets

The wax obtained as a residue in the extraction of the essence from English violets, *Viola odorata,* L., with volatile solvents, has been assayed by Louveau. The following constants have been recorded: $\text{density}_{15°}$ 0.962–0.966; melting point 58–61°; acid value 12.2–14.4; ester value 53.2–55; hydrocarbons 44–45.8 per cent.

Giacomello in Italy reported that the unsaponifiable fraction of the wax of violets, *Viola spp.,* L., contains a wax of the composition $C_{30}H_{50}O$, m. 284.5°, density 1.076, and has been identified as a triterpene with an esterogenic action. *Nonenol,* $C_{19}H_{17}OH$, has been reported by Taki, *et al.* as a constituent.

Wax From Acacia Flowers

The wax of two species of acacia has been reported on, that of *Acacia cavenia* and *Acacia dealbata.* These waxes according to Louveau are residues of the essence extracted from the flowers of these species, which are members of the family *Mimosaceae.* Mimosa wax appears to be of similar order. It is probable that the cassia-flower tree, *Acacia farnesiana,* Willd., whose flowers are much used in perfumery would yield a similar wax. The constants for *A. cavenia* are: $\text{density}_{15°}$ 0.946; melting point 55°; acid value 6.3–7; ester value 52.5; hydrocarbons 29.8 per cent. The constants for *A. dealbata* are: $\text{density}_{15°}$ 0.962–0.969; melting point 59–61°; acid value 24.8–25.2; ester value 78.9–89; hydrocarbons 47–49 per cent.

Jasmine Flower Wax

Jasmine flower wax has been prepared in Japan from the shuei flower; that is the sweet-scented yellow jasmine, *Jasminum odoratissimum*, L. The flower is cultivated in Formosa, and is noted for its fragrance. From 90 kilos of fresh flowers were obtained 250 grams of essence by extraction with petroleum ether, and then evaporating the ether. The essence (0.28 per cent) was separated into oil, the yield being 0.116 per cent; and into the flower wax in an equivalent amount.

Shuei flower wax has a specific gravity of 0.8259 at 100°/15°; refractive index *n* 60/D of 1.4622; optical rotation $[\alpha]\frac{18}{\mathrm{D}}+0.11$; acid value 1.25; saponification value 67.5; unsaponifiable matter 67.1 per cent; iodine number (Hübl) 100; Reichert-Meissl number 1.0; and melting point 45–57°. It contains 67 per cent of *triacontane*, $C_{30}H_{62}$.

According to Louveau the constants for the wax of large-flowered white jasmine, *Jasminum grandiflorum*, L., are: $\text{density}_{15^\circ}$ 0.950–0.971; melting point 61–64°; acid value 6–7.6; ester value 56.8–60; hydrocarbons 40–44 per cent.

Syringa Flower Wax

Radcliffe and Allan[112] have reported on the wax obtained from an extract of the petals of the syringa flower, *Philadelphus coronarius*, L. The wax is obtainable as a yellowish-brown substance possessing a slight odor resembling jasmine. They give the following constants: titer 56–57°; Zeiss butyro-refractometer readings, 30 at 84°, 33 at 74°, 36 at 70°, 38 at 65°, 40 at 62°, 44 at 56°: acid value 2.8; saponification value 65.8. Amyl alcohol was used as a solvent for the wax in the determination of the saponification value. The iodine number is 52–53 (Wijs). The purified wax acids had a mean molecular weight of 398 and iodine number of 39. The unsaponifiable matter yielded a mass of white needles (from ether) m. 64°. The unsaponifiable contained alcohols but presumably consisted mostly of hydrocarbons.

Butea Flower Wax

Butea frondosa, Roxb., also known as the dhak tree, indigenous from India to Burma furnishes the inspissated sap Palas Kino gum, seeds which are the source of Moodooga oil, and flowers (keeso, teeso) used for dyeing. The tree also yields lac. When the flowers are extracted with petroleum ether, and the extract dried and taken up with acetone, 0.75 per cent of a nearly colorless wax, results, having a melting point of 73–76°. Carbon tetrachloride yielded 0.35 per cent of a wax, which after repeated solution and precipitation with ethanol, had a density$_{15°}$ 0.980; acid value 6.2; saponification value 40.8; iodine number 1.2; and unsaponifiable 70.0 per cent. The colorless substance, crystallized from ethanol and ether had a melting point of 83–85°. This waxy substance proved to be principally *myricyl alcohol*. Fatty acids identified were *stearic* and *palmitic*, accompanied by *arachidic* and *lignoceric*. *Sterols* are also thought to be components.

Hyacinth Flower Wax

Blossoms of *Muscari botryanthus*, Mill., or allied species of hyacinth belonging to the family of *Lilliaceæ*, contain a wax. The wax is obtainable by extracting the dried residue left after exhaustion of the blossoms with ethanol to produce the perfume essence. The petroleum ether extract after distilling off the solvent leaves a soft wax of greenish yellow color, which has a somewhat larger proportion of esters of unsaturated acids and a lower melting point than other floral waxes.

The following constants were recorded by Straman[130a] for a wax of the above description, which was secured from perfume manufacturers in France and Holland: density 0.956$_{15°}$, melting point 48°, acid value 2.2, ester value 102.7, saponification value 104.9, iodine number 55.8, hydrocarbons 25.4 per cent, higher alcohols 25.0 per cent, saturated acids 27.7 per cent, unsaturated acids 19.1 per cent.

Pongamia Flower Wax

The ligroin extract of the flowers of *Pongamia glabra*, Vent., which is indigenous from India to Australia, and the Fiji Islands, is made up of waxy matter, some oil, and a small amount of a colorless crystalline substance m. 212°, which is known as *pongamin*. Murti and Seshadri[106a] state that the aliphatic waxy portion consists mostly of esters derived from C_{24} to C_{34} alcohols and C_{24} to C_{30} acids, and about 12 per cent of hydrocarbons, C_{27} to C_{33}.

Clover Flower Wax

The dried flowering tops of the carnation or crimson clover, *Trifolium incarnatum*, L., were extracted by Rogerson[116a] with alcohol, and the extract then distilled with steam to secure 0.029 per cent of essential oil. From the portion insoluble in alcohol he obtained a wax which contained *incarnatyl alcohol*, $C_{34}H_{69}OH$, which had been previously isolated from the wax of the humble bee (see p. 60); *hentricontane*, *1-phytosterol* (same as that from jambul seed) m. 135–136°, $[\alpha]_D$–41.7; *trifolianol*; *palmitic*, *stearic*, *linolic*, and smaller amounts of *oleic* and *isolinolenic* acids.

Part IV: Waxes from Gum-Resins

Occurrence of Waxes in Gum-Resins

Fossil resins do not contain wax. Resins of recent origin may in some instances contain a small proportion of wax, and the properties of the gum-resin are improved by putting it through a process of dewaxing, in much the same manner as stick-lac is dewaxed to produce the shellac of commerce. Damar gum-resin is dewaxed on an extensive scale to produce desirable grades of damar resin for the varnish industry, and the damar wax becomes a by-product. Like shellac, wax is reintroduced in suitable proportion to obtain special shellacs; damar wax is also put back in certain varnishes to obtain a flat finish. However damar wax has been available to a limited extent for use in wax mixtures to improve hardness and melting point.

Damar Wax. The damars are customarily designated from the point of entrance into commerce as Batavian damar, and Singapore damar. In general the damars originate in the East Indies. They are compatible with other resins, waxes, stearic acid, pitch, cellulose derivatives, and oils. They are alcohol-insoluble but soluble in all hydrocarbon solvents. However, damar resin is not completely compatible with the solvents used in the cellulose lacquer industry and it is necessary to remove a constituent beta-resene, which occurs to the extent of 8 to 10 per cent, to make the damar useful.[6]

The process of dewaxing damar gum-resin consists of dissolving it in a suitable solvent and then precipitating the wax by methanol, ethanol, or other alcohol, commonly denatured. For the better grades of damar, good results in dewaxing are obtained by dissolving the gum-resin in an equal weight of toluene and adding an equivalent weight of alcohol. For the poorer grades the toluene may be replaced by a mixture of $\frac{2}{3}$ petroleum naphtha and $\frac{1}{3}$ ethyl acetate, or by ethyl acetate 12.5, acetone 12.5, and benzene 75 parts. By increasing the proportion of damar $2\frac{1}{2}$ parts to 2 parts solvent, *i.e.*, toluene and alcohol 1 : 1, good results are obtained with all grades of damar.

Damar wax is soluble in all naphthas—paraffinic, naphthenic or hydrogenated. The wax is soluble in terpineol to a viscous gel. It is freely soluble in turpentine, and to a lesser extent in coal tar solvents and tetralin, and insoluble in the usual lacquer type solvents. Damar wax is insoluble in all alcohols, inclusive of isopropyl, butyl, amyl, and benzyl. It is insoluble in ethers, esters, and many ketones including diacetone.

Damar wax when purified by reprecipitation is a brittle white material of a very low acid value, namely 2–4. It melts at 200–210° (392–410° F). If damar wax is cooked with linseed oil a viscous product like the heaviest type of lithographic varnish results. This property can be made use of in giving a false body to varnishes and enamels when so desired. The very high melting point of damar wax makes it useful as a "booster" for the melting point of other waxes.

Part V: Waxes from Micro-organisms

Adipocere Wax

The term *adipocere* is given to wax found on post mortem examination of vegetable or animal substances, which results from putrefaction by micro-organisms. For example the wax produced by thermolabile bacteriotoxins in the soil, may be extracted with wax solvents. The soil particles are covered with a wax layer non-saponifiable and partly saponifiable in nature. In soil this toxic substance is referred to as "agrica" and it stifles plant life, but with the wax extracted it apparently promotes it, according to Greig-Smith. Cottage cheese and lean meat are said to produce slight amounts of fatty waxes on putrefaction. Adipocere is occasionally found in tissues particularly where the human has been a victim of disease and the fat has been formed in the various tissues. Adipocere wax is encountered in the decomposition of corpses in cemeteries. The wax consists of a mixture of fatty acids, probably *palmitic*, and *stearic*, with their calcium soaps. Traces of various minerals are present as impurities. Varieties of *hydroxystearic acid* are also found in human and in pig adipocere.

The alcohol obtained from the fat of dermoid cysts termed cetyl alcohol is an *eicosyl alcohol* of the formula $C_{20}H_{42}O$, m. 70°. On oxidation it yields *arachidic acid*, m. 73°.

Human Tubercle Bacillus Wax

Human tubercle bacilli contain lipoids, and lipids both fatty and waxy. In 1901 Kresling[77] reported that in extracting dried tubercle bacilli with chloroform he obtained fatty substances (lipids) which were composed of 14.4 per cent of free fatty acids, 77.2 per cent of neutral fats and fat acid esters, 0.16 per cent of lecithin, and 0.70 per cent of water-soluble substances. The fat acid esters contained 31.9 per cent of alcohols, m. 43.5°. The total fatty matter had the following constants: melting point 46, acid value 23.1,. Reichert-Meissl value 2.0, fatty acids plus unsaponifiable 74.2 per cent, saponification value 60.7, and iodine number 9.9.

Bullock and Macleod[23] in 1904 reported that they had extracted the dry tubercle bacilli with Aronson's mixture (a mixture of alcohol and ether containing 1 per cent HCl), and saponified the fatty substances (lipids) with sodium alcoholate. The wax which escaped saponification was examined by Lewkowitsch who found it to have an iodine number 9.4, saponification value 49.4, melting point 4.4°, and acetyl value 69.0. He believed lecithin, a higher alcohol (not cholesterol), and palmitic acid to be the chief constituents of the wax.

In 1910 Fontes,[44] of Rio de Janeiro, extracted dry tubercle bacilli with xylene, ethanol, ether, and chloroform, in successive stages by means of a Soxhlet apparatus. The xylene extract on the addition of alcohol gave a precipitate soluble in the fat solvents, and consisting of microscopic refractive amorphous granules, stainable by Ziehl's solution and acid-fast. Saponification of this material proved it to be a wax. When the distillate of the xylene-ethanol filtrate was brought into barium hydroxide solution and the resulting precipitate decomposed by sulfuric acid, no fats were indicated. The wax melted at 54.5°, the chloroform-soluble part at 193°. *Palmitic acid* was identified as a water-precipitable saponifiable fatty acid in the xylene-alcohol mixture.

The presence of *mycolic acid* as the principal constituent of the wax lipid of tubercle bacilli was revealed by the investigations of Stodola, Lesuk and Anderson[130] in 1908. They proposed the name for the saturated hydroxy methoxy acid of high molecular weight which they had isolated. Mycolic acid does not crystallize, and is difficult to purify. Its composition is $C_{88}H_{172}O_4$ or $C_{88}H_{176}O_4$. It is optically active $[\alpha]\frac{20}{D} = 1.8$ in chloroform, and melts at 54–56°. When heated it is decomposed into *n*-hexacosanic acid, $C_{26}H_{52}O_2$ and a non-volatile residue.

In 1927 Anderson[3] extracted the lipoids from moist living tubercle bacilli at room temperature with a mixture of ethanol and ether, followed by an extraction with chloroform. To prevent oxidation, air was rigidly excluded by using an atmosphere of carbon dioxide. Three fractions were obtained, consisting of glycerides, phosphatides, and wax, the wax constituting more than half of the lipids. Over 2000 cultures were used, each culture containing nearly 2 grams of dry bacteria, and the total lipoid material represented 23.8 per cent of the bacilli. The chloroform-soluble wax amounted to 427 grams. In 1929 Anderson reported that the purified waxy matter is a white powder, m. 200–205°, yielding 71 per cent of ether-soluble and nearly 40 per cent of water-soluble constituents on hydrolysis. Approximately 56 per cent of the total waxy matter consists of a snow white powder, possessing both acid and alcoholic properties, which is designated "unsaponifiable wax." The water-soluble constituents consist of glycerophosphoric acid, a mixture of reducing sugars, etc. Therefore the purified material is principally a complex phosphatide containing a large amount of carbohydrate.

Later in 1929 Anderson and Chargaff,[4] by fractional distillation of the methyl esters of the liquid fatty acids occurring in the acetone-soluble fat obtained from tubercle bacilli, isolated two new fatty acids. The first was named *tuberculostearic acid.* It is isomeric with stearic acid, is liquid at room temperature, and is optically and biologically inactive. The other acid was named *phthioic acid.* It melts at 28°, $[\alpha]\frac{20}{D} = 7.98$, and is isomeric with cerotic acid. It is biologically active. The unsaponifiable wax from the tubercle bacilli liberates *hexacosanic acid* when distilled in a high vacuum.

Summing up, the wax fractions extractable from tubercle bacilli yield a complex mixture of fat and wax acids on saponification: (a) normal saturated acids—*palmitic, stearic,* and *hexcosanic*; (b) saturated branched chain acids—*tuberculostearic,* phthioic, and an 1 acid $C_{31}H_{60}O_2$; (c) unsaturated acids above C_{20} yielding hexacosanic acid on hydrogenation, and (d) *mycolic acid.* All wax fractions contain the hydroxyl alcohol, *phthiocerol* $C_{35}H_{72}O_3$, together with water-soluble matter, such as carbohydrates and glycerol.

Avian Tubercle Bacillus Wax. Avian tubercle bacillus wax, according to Reeves and Anderson,[114] constitutes 70.7 per cent of the total lipids and 10.8 per cent of the dried bacterial mass.

After the wax had been purified and saponified the cleavage products were found to consist of fatty acids, unsaponifiable matter and a water-soluble carbohydrate.

The fatty acids were a complex mixture of optically active hydroxy acids of very high molecular weight whose constitution could not be determined.

The unsaponifiable consisted mainly of *d-eicosanol-2* together with a small amount of *d-octadecanol-2.* The water-soluble carbohydrate was identified as trehalose.

Human tubercle bacillus contains a similar wax, and in the unsaponifiable matter, the dihydric alcohol, *phthiocerol* ($C_{35}H_{72}O_3$) had been previously identified. Avian wax resembles timothy bacillus wax, both containing the previously mentioned constituents.

The crude wax is a non-crystalline powder of light yellow color. It is soluble in chloroform, ether, benzene, toluene, ligroin and ethyl acetate, but insoluble in acetone, ethanol and methanol. It has a melting point 53–54°, iodine number 7.8, saponification value 77, $[\alpha]_D$ in chloroform $+25.6$. The purified wax is a white granular powder $[\alpha]_D$ 38.6, melting point 54–55°, iodine number 4.5.

The wax acids approximate $C_{38}H_{74}O_2$ in composition, and melt at 69–70°, methyl ester 54–55°, iodine number 6.5.

Lipid Waxes

Lipids are naturally occurring substances that are grouped together because of similarities in solubility (common solubility in fats solvents) and common capacity of being utilized by living organisms. There are simple lipids and complex lipids (lipins). Waxes that are lipids are classified with fats and oils as simple lipids. The lipid waxes are esters of monohydric alcohols (either aliphatic or cyclic) with high molecular weight aliphatic carboxylic acids. They are commonly distributed in the plant and animal kingdoms.

The lowest straight-chain alcohol derived from lipid waxes by hydrolysis is *lauryl alcohol* and the highest is possibly *melissyl alcohol.* The lower alcohols are largely associated with liquid waxes mostly of marine origin, and include unsaturated alcohols as exemplified by *oleyl alcohol* and *linoleyl alcohol.* The sterols in lipid waxes are usually isolated by ether or chloroform extraction of the unsaponifiable portion of a lipid fraction. They include *agnosterol* of wool fat, *cholesterol* in animal cells, *ergosterol* of yeast, *fucosterol* of algae, *α-sitosterol* in the fats of higher plants, *stigmasterol* of soy bean and sugar cane, etc.

The lipid waxes are intimately associated with the metabolism in which lipolytic enzymes function, but the mechanism of the reactions is not so well known. The sterols derived from yeast and fungi are termed *mycosterols.* An example of a mycosterol is *zymosterol,* $C_{27}H_{43}(OH)$, found in yeast.

The unsaponifiable fraction of grapeseed oil contains 14.8 per cent of sterols, including *phytosterols, α-sitosterol, ergosterol D, dihydroergosterol, β-amyrin* and traces of *tocopherols.*

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Chapter 4

Fossil Waxes, Earth Waxes and Lignite Paraffins

FOSSIL WAXES

Algae Wax

Algae wax is a fossil wax produced by algae, according to Kramer and Pontonié, who in 1906–1907 advanced the algae hypothesis of the vegetable origin of petroleum. They pointed out that all petroleums—also certain liquites and ozocerite—contain algae wax; this wax, by various reactions and decompositions, is easily converted into a substance like petroleum. Simple substances, by polymerization through the instrument of heat and pressure, form more complex tarry substances, etc. The presence of the wax, they contend, demonstrates that petroleum is not formed in the hot by distillation but rather in the cold at high pressure.

Let us consider for a moment the waxy constituents of living algae. Algae such as zooplankton and phytoplankton contain 17.3 and 15.5 per cent respectively of saturated acids of high molecular weight, and 53.2 and 2.1 per cent respectively of highly unsaturated acids. The chlorophyceae contain C_{14} to C_{18} saturated acids, and C_{14} to C_{22} unsaturated acids. These living micro plant organisms fossilize eventually so that the unsaturated acids disappear, and wax esters form along with the hydrocarbons.

Hilditch[7] states that seaweed wax is obtained from deposits of algae which have been converted into material analogous to peat or lignite, and that the wax contains esters of the higher saturated alcohols and fatty acids of the C_{20}, C_{22}, and C_{24} series; that is, *eicosanic, docosanic* and *tetracosanic acids*. These acids are also commonly called *arachidic, behenic,* and *lignoceric acids*. A sterol found in the lipid wax of living algae is *fucosterol* $C_{29}H_{47}OH$, m. 124°, ($[\alpha]_D - 38.4$).

Kramer and Pontonié hypothesized that the primary material of petroleum was the algae which were abundantly laid down in all epochs and which are today accumulating in marshy places. These algae, during thousands of centuries under the action of pressure and heat, could undergo transformations and putrefactions, leaving a wax which is converted into petroleum. In this manner, petroleum would be formed through the years, and is perhaps being formed now. Whether this algae wax is identical with the "soft wax," which in small percentages causes paraffin to change from a plate to needle crystalline structure, or in large quantities brings about an amorphous structure in waxes produced from long residuums, is a subject of speculation.

Legg and Wheeler[8] found that the wax of fossil plant cuticles from Russian *papierkohle* consists chiefly of *oleic* and saturated *hydroxyaliphatic acids*; they obtained a yield of 4 per cent. They attempted to relate this to the waxes from modern plant cuticles, such as those of the century plant, *Agave americana*, L., and those of the sisal-hemp plant, *Agave rigida*, Mill., and found a similarity in the respective combustion products.

The wax of the *Agave rigida* cuticle contains 85 per cent of alcohols, principally *montanyl* and *mellisyl* alcohols.

Hydrocarbons $C_{18}H_{36}$, $C_{20}H_{34}$, $C_{21}H_{38}$ and unsaturated terpenes have been found in brown algae, such as *Alaria crassifolia*, Kjellm, upon extraction with petroleum ether.

The Galician beds have been worked at great depths, 1000 feet or more, and the deeper the mining the softer and more paraffin-like the ozocerite. In Utah on the other hand the mineral wax is removed from thin stringers and veins up to one foot or so in thickness, and is quite hard. Peculiarly the paraffin "scale" deposited on the casing of certain wells in Trinidad and elsewhere appears to be similar in nature and of approximately the same melting point.

The mining of ozocerite in Galicia is comparatively simple. Formerly merely well shafts were sunk, but today it is mined in the manner of coal, by deep underground operations. The mined ozocerite is dark in color, the lumps intermingled with earthy impurities; it is cleaned by hand, or by melting. Boryslaw wax thus melted is cast into forms resembling truncated cones that weigh about 40 kilograms, and brought into commerce. The qualities produced at the mine are the "hardgreen," "hardbrown," and "softblack," which are graded by the following congealing points: "hardgreen," 74–76°, 70–72°, and 66–68°; "hardbrown," 70–72°, and 66–68°; "softblack," 55°. The melting points are 4° above the congealing points.

The cleaned crude ozocerite has an amorphoid or microcrystalline structure, and a density of 0.900 to 0.907 at 15°. The bleached ozocerite has a similar physical structure but is of a little higher density, namely 0.910 to 0.920 at 15°.

EARTH WAXES

Natural Occurrence of the Earth Waxes

The earth waxes, often referred to as ozocerites, may be designated as naturally occurring mineral waxes consisting of an aliphatic series of straight chain and branched-chain hydrocarbons, with some oxygenated resinous bodies. What is known commercially as *ozocerite* is the particular earth wax that is mined in Eastern Europe. The earth waxes found elsewhere, as for example in the United States, are of a somewhat different hydrocarbon composition from ozocerite, and exhibit differences in their physical behavior.

The earth waxes are in many respects similar to microcrystalline petroleum waxes, occurring in a natural state instead of being artificially produced by the destructive distillation of petroleum. The origin of earth waxes is believed to be closely linked to the origin of petroleum, which is derived from the carbonization and concomitant distillation of animal or vegetable remains, under the heat and great pressure deep under the earth's surface, during one of the middle epochs in geological history. One theory is that petroleum in many regions was forced by hydrostatic pressure upward through porous sandstone capped by impervious shale.

Specimens of earth waxes have been obtained from Scotland, Northumberland, and Wales, as well as from Russia (the Kaukasus, Tscheleks, Turkestan), and from Iran (Fergona). The largest workable deposits are those of ozocerite in the Carpathian Mountains. In the United States a considerable tonnage of earth wax is being mined at Soldiers Summit, Utah. There are also deposits of earth waxes in South America.

Ozocerite

Ozocerite, also spelled as it is pronounced—ozokerite—is a name apparently derived from the Greek words *ozo* "to emit odor," and *kerite* which is "wax." About the middle of the last century, it is said, came news from Galicia of the existence of a natural earth wax, which had some of the characteristics of beeswax. At or near its source it had been used for many years for the making of axle grease, leather dressing, and as a fuel for heating.

In Galicia sources of commercial supply are at Boryslaw, Dweiniacz, and Starunia. The largest mines are those of the northern foothills of the Carpathians, particularly in Boryslaw near Drohobycz. Abundant deposits are also found in the Wallachian side of the range, and in smaller deposits along the Caspian under the name of "neft-gil." It is said that at one time there was as much as 20,000 tons per annum mined in Galicia, but the production is far less than that amount at the present time.

Where ozocerite is found the shale is soft and it is believed that the shale in geological ages acted as a molecular filter and condensator. According to one hypothesis, small hydrocarbon molecules were converted into large ones by a sort of polymerization process leaving a residue of wax, which occasionally is accompanied by small amounts of oil. The colloidal earth which accompanies ozocerite is salty, which indicates the existence in an early geological era, probably carboniferous, of a water hydrostatic pressure. The greater the pressure to which ozocerite has been exposed, the lighter its color and greater its hardness. We would expect and do find the hardest wax (marble wax) to be pressed up against the overlying rock.

Refining of Ozocerite. In 1870 Pilt and Ujhelyi found that a simple treatment of mined ozocerite with concentrated sulfuric acid, followed by decolorization with animal charcoal, yielded a product of great value in the arts and industries. Molinari has described the refining process as follows: "The refining is carried out in large iron boilers holding up to 3000 kilos of the crude wax, which has been melted free from earthy and stony matter at the mines, half a meter being left free to take the sum which forms. The fused mass is kept at 115–120° for 4 to 5 hours and is stirred to liberate all the water; 15 to 25 per cent (according to the quality of the wax) of fuming sulfuric acid containing 78 per cent of SO_3 is then added in a thin stream to the mass, which is thoroughly stirred meanwhile; the temperature slowly rises to 165°, then to 175°, the oxidizable impurities separating as a black asphaltic mass, and the excess of sulfuric acid evaporating. The vessel is covered and provided with a draught-pipe to carry off the acid vapors. The mass is allowed to cool slowly, being neutralized with residues from the manufacture of ferrocyanide, decolorized with animal black and sent to the filter presses. The mass obtained is still slightly yellow and is whitened by further treatment with sulfuric acid. When beeswax is to be imitated, quinoline yellow or other suitable coal-tar dye is added."

Acid treated ozocerite which has received no additional decolorizing treatment is referred to as *yellow refined ozocerite,* or *once bleached ozocerite.* The fully refined wax is known as *double bleached,* or *white refined ozocerite.*

No bleaching of ozocerite is conducted at Boryslaw, Poland. The black wax reaches the port of Trieste, or Fiume, and from there is exported elsewhere. The wax bleached in Italy became known as "ceresin," but it was very often blended with white refined paraffins before being exported to other countries.

Ozocerite crude on distillation in a current of superheated steam yields a candle-making material resembling paraffin obtained from petroleum and shale oil, but of higher melting point (64–65°) than ordinary paraffin, and therefore of greater value if the candles made from it are to be used in hot climates. There are also obtained in the same distillation light oils and a product resembling "Vaseline." The residue left in the stills consists of a hard black waxy substance, which when incorporated with india rubber is employed under the name of *Okonite* as an electrical insulator.

From the residue a form of material known as *heel-ball*, used to impart a polished surface to the heels and soles of boots, is also manufactured.

There is probably no wax which is subjected to adulteration as much as ozocerite. Therefore, methods of detecting such adulteration are worthy of consideration when this wax is purchased from any other than a very reliable source. The melting point, the specific weight, and the structure, *i.e.* the feel of an ozocerite, are determinants. The addition of small amounts of paraffin, 5–10 per cent, to ozocerite almost defies detection, since ozocerite itself differs slightly in its physical constants depending upon its origin.

Physical Properties of Ozocerite. *Pure white ozocerite* when compounded with crystalline *paraffin* of 128–130° F melting point in the proportion of 1 to 3 produces a wax melting at 158° F. The latter mixture has very much the same properties as ozocerite except for the somewhat lowered melting point, and is much less expensive. There is unfortunately a great temptation to adulterate ozocerite with a proportion of paraffin and to undersell jobbers marketing the 100 per cent pure ozocerite.

When it is desired to substantially change the macrocrystalline needle structure of paraffin to a plate microcrystalline structure, 5–15 parts of ozocerite may be added to the paraffin; 25 parts of the ozocerite will completely destroy the crystalline needle structure of paraffin.

Pawleski[15] studied the behavior of ozocerite with solvents. The ozocerite paraffin was one that had been distilled in a current of superheated steam from the crude. It had a gravity of 0.9170 at 20°, melted at 64–65°, and solidified at 61–63°. One hundred cc of solvent dissolved the following amounts of ozocerite wax expressed in grams: petroleum ether 8.48, turpentine 5.21, cumene 3.72, xylene 3.43, toluene 3.34, chloroform 3.61, benzene 1.75, isobutyl alcohol 0.228, acetone 0.209, amyl alcohol 0.164, methanol 0.056, glacial acetic acid 0.063, formic acid 0.015. The following weights of solvent were required to dissolve completely 1 part of ozocerite wax: carbon disulfide 7.6, petroleum ether (b. p. up to 75°) 8.5, turpentine 16.1, xylene (b. p. 135–143°) 25.1, toluene (b. p. 108–110°) 26.1, chloroform 41.3, benzene 50.3, ethyl ether 50.8, isobutyl alcohol 352.9, acetone 378.7, ethyl acetate 419.0, ethanol 453.6, methanol 1447.5, methyl formate 1648.7.

On the whole ozocerite is much less soluble in various solvents than paraffin wax. Carbon tetrachloride (100 ml) dissolves 11.78 grams of of paraffin (130° F m. p.), but only 1.95 grams of ozocerite. Chloroform, amyl alcohol, benzene, acetone, and ether all dissolve nearly five times as much paraffin as ozocerite.

Ozocerite has an excellent moisture resistance, a low index of refraction, and a very low conductance for heat. Its coefficient of expansion is

0.001 per 1°, between 1° and 50°. The melting point of pure Galician ozocerite is 73° (163° F), cloud point 76° (169° F), boiling point above 300° (572° F). The dielectric strength is in excess of 30,000 volts across a 1/10 inch G. E. standard gap. Its dielectric constant (permativity) is 2.03; its power factor 0.03; and resistivity 36×10^6 megohms across a 1 cm cube.

A pure white refined form of Galician ozocerite that has appeared on the market is known under the trade name of *JAA Wax,* the initials being impressed on each slab as not to mistake its identity. JAA Wax has a melting point of 75° (167° F). Pure white ozocerite in the melted form has a much lower specific gravity (0.753–0.796 at 98°) than beeswax (0.822), and contains no saponifiable matter.

Hardness of Earth Waxes. The hardness of the earth waxes varies a great deal according to the source and whether they are crude or refined, the latter being softer. An approximation of the hardness may be determined with the aid of a Shore durometer (scale 0–100).[26]

Earth Waxes	Durometer Hardness at 25°
Ebony Utahwax	95
Still Run Utahwax	
No. 1	90
No. 2	85
No. 3	80
Refined Yellow	70
Galician Pure White	53
Ceresin-made with	
⅔ Paraffin of 123–125° F m. p.	55
⅔ Paraffin of 128–130° F m. p.	60
Miscellaneous Waxes (for comparison)	
Carnauba wax	97
Bleached Beeswax	60
Paraffin of 123–125° F m.p.	55
Paraffin of 128–130° F m.p.	65
Microcrystalline Petroleum Waxes:	
"Petrowax" (yellow)	20
"B-Square White"	50
Yellow (160° F m.p.)	50
Black (160° F m.p.)	50
Black (180° F m.p.)	85

The addition of paraffin of 128/130° F melting point to ozocerite increases its hardness and its toughness. The waxes compounded from paraffin and ozocerite when properly proportioned have a dense microcrystalline structure much desired for many purposes. For most purposes paraffin wax of 128–130° F melting point is also greatly improved in its physical characteristics by the addition of ozocerite.

Chemical Composition of Ozocerite. Ozocerite is composed of both cyclic and paraffinic hydrocarbons. It is thought that it has large polymethylene rings which might be considered as double chains. Ceresins, of which Boryslaw ozocerite is a type, retain their oil very tenaciously and cannot be separated therefrom by the usual process of filtering and pressing. At similar melting points, the ceresins have a much higher molecular weight, specific gravity, viscosity, boiling point and nitrobenzene points than the paraffins. They have a delicate crystalline structure, the crystals being of needle or short plate shape, microcrystalline. Chemically the ceresins are much less stable than solid paraffins and react readily with fuming sulfuric acid or with chlorosulfuric acid, a fact which has been interpreted to indicate an isoparaffinic structure. On account of their high boiling points they can be partially separated from paraffin wax. Molecular weights corresponding to the formulas $C_{37}H_{76}$ to $C_{53}H_{108}$ are found for these branched chain hydrocarbons. The monoclinic needle-like variety of crystals are believed to consist of open chain paraffins with short branches, and the triclinic plates of saturated cyclic hydrocarbons with long chains.

Use of Ozocerite in Industry. Ozocerite easily mixes on melting with oils and fats of most any description, and with waxes such as paraffin, carnauba, japan, bees, montan, etc. It mixes with stearin, asphaltum, and rosin. It readily dissolves in distillates from coal or petroleum, producing on cooling a product of salve-like consistency. Of all the waxes it has the greatest affinity for oil, or absorbs it the best. Ozocerite, because of its many valuable properties, is extensively used in many industries.

A good shoe polish or cream should be of a salve-like consistency, should not exude oil, and should produce a brilliant gloss. The luster of such a polish is furnished by hard waxes like carnauba but the salve-like consistency and oil retaining quality are best obtained from ozocerite. Paraffin wax, when used as a cheap substitute in paste polish, may cause cracking around the edges of the box, after the paste dries through exudation of the oil. This is also true of paraffin wax in floor polishes and leather dressings.

In the manufacture of pharmaceutical and cosmetic preparations it is highly desirous to use a neutral white, odorless, tasteless, amorphous wax. Ozocerite is of great value in these preparations. The electrical industry has always been a large consumer of ozocerite, crude or refined, as it is an excellent insulator. The surface resistance is said to be three to seven times that of ordinary paraffin wax and the transient resistance 220 to 1700 times greater. The crude or refined wax is used in accumulators, dry batteries, cable boxes, and dynamo armatures. Certain hard rubber compounds for electrical purposes contain 2–5 per cent ozocerite. Ozocerite makes an excellent cable-wax because of its durability, elasticity, resistance to marked changes in temperature, and its insulating properties. In cable coating the ozocerite is preheated for several hours at a high temperature before applying it to the cable.

Fat compounds prepared from paraffin and tallow, or the like, are used in their melted state to impart to tanned leather a polish, color, moistureproofness, elasticity, and toughness. By adding ozocerite to these compounds they can be greatly improved, resulting in a better quality of leather with increased weight. It also prevents the paraffin wax and stearin from causing a bloom or spew after the leather has been drawn through the bath. It is advantageous to add as much as 25–30 per cent to the fat compounds.

In wax figure making ozocerite can be freely substituted for beeswax, and hence is of great value in that art. Its high melting point is advantageous. Hard paraffin waxes when used for this purpose prove unsatisfactory as they are dry and brittle and are apt to scale off. Ozocerite is also used in the making of tapers and candles.

Paper converters find ozocerite of value in the preparation of glassines, carbon paper, waxed paper, waxed oil paper, etc. Ozocerite is used in the manufacture of wax flowers, crayons, waxed matches, for impregnating corks and umbrella silk, and for steam packings. The "hard green" variety is used by the electrotypers to secure sharp impressions, since this type of wax has a low coefficient of expansion and contraction.

Ozocerite is used in waterproofing cloth; the treatment forms one step in the finishing. The waterproofing solution may be of the following formulation: ozocerite 5, liquid petrolatum 5, and benzene 90 parts. After evaporation of the benzene the waterproofing material contracts on the yarn, and leaves the pores of the cloth free and open, a desirable part of the finish. The waterproofing of pails, casks, and other vessels and utensils by ozocerite was patented as early as 1885 by Maxfield.[11]

Artificial Ozocerites. Artificial ozocerites are made in Germany as products of the Fischer-Tropsch benzine synthesis, as reported by Nitsche.[14] Such products have been made in various consistencies, from tallow soft with 58° melting point, to hard having a 77° melting point. They are said to behave like pure Polish ozocerite in homogenizing the wax structure of a wax-solvent paste. They restrain any visible crystallization at the surface of paraffin pastes, and the solvent of the paste is readily freed. Nitsche advocates using adsorbent agents in preference to acid in the refining of ozocerite, since by so doing there is less danger of harming the homogenizing properties of the ozocerite as it is bleached.

American artificial ozocerites going under the trade name of Ozotex, are amorphoid waxes derived from American petroleum by centrifuging certain still residues extracted with selective solvents. The substitute waxes are supplied in 160 to 165° F melting point, with a fair degree of plasticity, and also in harder higher melting point numbers, such as 180 to 185° F.

American Mineral Wax. About fifteen hydrocarbons occur in Utah, five of which are well known; namely, gilsonite, tabbyite, wutzellite, ozocerite, and rock asphalt. Gilsonite is limited to Uintah County, where it occurs as a filling in vertical fissures in the Green River calcareous shales of the Eocene period, limestones, and sandstones. Tabbyite occurs in Tabby Canyon, Uintah County, in vertical fissures in Upper Tertiary sandstones and shales. Wutzellite, also known as elaterite or mineral rubber, occurs in an area between Indian Canyon and Sam's Canyon, north of Price, in vertical veins one to twenty-one inches wide. Utah ozocerite, also known as American mineral wax or more specifically *Utahwax*, occurs in an area west of Cotton, Utah County, in shales, shaly sandstones, and limestones, in the lower part of the Wasatch Tertiary Formation, chiefly in fissures and spaces in zones of brecciation and jointing. Rock asphalt, or bituminous sandstone, occurs in large deposits in many localities. The various hydrocarbons are mentioned since there may be a genetic relation among them.[1]

A considerable amount of Utahwax, as the Utah ozocerite has been termed, is being mined by breaking it out of the seams with a pick, unlike the open mine method of winning ozocerite in Europe. In the deeper workings in the Utah mine the ore is brought to the surface and milled. It is then melted and refined later at the refinery to which the crude is shipped. The ore is of a black-brown color, and the first melts are black. The Ozokerite Mining Co., of Grand Rapids, Michigan, works on a Utah mineral wax ore which melts at about 93° (200° F). This is acid bleached to prepare uniform gradings for the market. Grades which have come to the writer's attention are "Ebony Utahwax," "Still Run Utah No. 1," "No. 2," and "No. 3," and a "Refined Yellow." The "Ebony" is the hardest and the "Refined Yellow" the softest of the gradings. The latter is sometimes referred to as "Double-Refined Plastic Utahwax, and it is rather orange-yellow in color. The structure of the waxes is microcrystalline but nearly amorphous.

Measurements of hardness of Utahwax by penetrometer with standard needle, 100 grams weight, 15 seconds time, are given by the refiner as follows:

Temperature (°C)	Penetration (mm)
20	0.43
30	0.64
40	1.27
50	2.20
60	3.80

To illustrate the toughness of the wax a 9 mm jacketed bullet fired with a velocity of 1400 feet per second at a 5 inch thick slab penetrated one inch and was shattered into fragments without cracking the slab.

With a Shore durometer the writer determined the hardness of the Ebony Utahwax as 95 at 73° F. The durometer hardness of Still Runs No. 1, No. 2, and No. 3, were 90, 85, and 80 respectively. The Refined Yellow was 70 in hardness. Utahwax has a density of 0.9414 at 6°, 0.9290 at 25°, and 0.8850 at 60°.

Utahwax can be substituted to a great extent for the imported ozocerite in many of the industries but not all. The imported ozocerite has certain peculiar physical properties which are non-existant in other waxes, as for example in wax blends where the ozocerite has a remarkable decrystallizing effect and prevents softening of the other wax components at temperatures below the melting point.

Utahwax is less expensive than imported ozocerite and is chiefly used for electrical insulations; for waterproofing pails, corks, and other vessels for steam packing, and washers; for impregnating fabrics, and for wax matches.

Paraffin Distillate from Bituminous Mineral

By the destructive distillation of brown coals and of lignite are obtained the paraffins used in Continental Europe, aside from any importations of petroleum paraffins from America or elsewhere. Closely allied to bituminous lignite is bituminous shale from which the English paraffin is refined. Unfortunately the terms "brown coal" and "lignite" have come to be used interchangeably. Commonly speaking, all the immature coals of a tertiary origin, whether black or brown, woody, amorphous, or having a conchoidal or cubical fracture, are called "lignites." Lignite is the French word for the woody type of coal. The great mass of German coal is not lignite in the sense of being a woody coal which splits up into slabs on drying, but an amorphous brown earthy substance or brown coal containing bands of lignite.

In the Saxony and Thüringia district in continental Europe the bituminous mineral is referred to as "pyropissite," and these deposits at one time were the source of a great paraffin industry. Molinari[13] states that the valuable source of wax had been squandered by distillation when it might have been extracted in much higher yield by the direct use of a suitable solvent, and the mass purified by treatment with fuming sulfuric acid. In fact montan wax, which is not paraffin, is now extracted in the manner described. Locally it is known as *bergwachs*, which translated is "mountain wax." Paraffins are refined on an extensive scale from the brown coal deposits in Upper Silesia.

Ukrainian Lignite Wax

Many attempts are being made to refine the detarred lignite extracted from the still residue obtained as a by-product in the low temperature distillation of lignite for production of light fuel oil. The use of activated carbon to bleach the detarred lignite wax has not proved satisfactory, and the use of powerful oxidizing agents in large amount proves uneconomical. Most of the investigative work has been done by Romansikii[20] and his associates, of the Academy of Science in Ukraine.

By one method detarred lignite wax is refined by oxidation with chromic anhydride in the presence of sulfuric acid, in three stages: the first stage at a temperature of 106–110° for 3 hours and 40 minutes, most of which time is absorbed in the slow addition of the chromic anhydride. the second stage lasting 2 hours and 20 minutes, and the third 3 hours and 25 minutes. At the end of the third stage, the mass is cooled, the chromic solution decanted and the wax washed with acid, and then with boiling water to free it from acid. The yield is 80 per cent by weight.

The oxidation with chromic anhydride results in partial decomposition of esters, oxidation of portions of non-saponifiable material and the formation of fatty acids of high molecular weight. Potassium chromate and sodium chromate have also been used as oxidizing agents, the detarred lignite wax being first melted in 42 per cent sulfuric acid heated to 105–110°, and the powdered dichromate added while the mass is stirred, the process taking 10–12 hours to completion. When sodium chromate is used, it may be added in solution form. The treatment with the dichromates requires three stages to complete the bleaching of the wax. The amount of dichromates used approximates 145–160 per cent of the weight of the wax. The final product has an Ubbelohde melting point of 85.6°.

Montan Wax

Montan wax, or montanin wax, is a bituminous wax, not a paraffin, which occurs in woody coals, lignites, and is extracted therefrom by means of a volatile solvent. Crude montan wax, or *montanin wax crude* as it is sometimes called, is brown or black, but in the refined state it is nearly white in color. The name *montan wax* generally applies to the wax obtained from a bituminous lignite, or bituminous shale, but a similar wax may be extracted from peat or brown coal, as will be seen later on. The customary solvent for extraction of the Saxon-Thüringian lignite is benzene.

In the von Boyen process, which was patented in 1901, the lignite is crushed or granulated and dried before it is extracted. This was the practice of at least six different works in Germany. The only process in which the bituminous lignite is treated in the natural damp state in which it is raised from the mine is that of Frank and Ziegler, known as the wet extraction process. In both processes benzene is used as the solvent. Thüringian lignite is treated with benzene at a temperature of 260° and a pressure of six atmospheres, and the wax produced has a high melting point. The carbonaceous matter left as a residue in the extraction process is briquetted for sale as a fuel. The crude bitumen or wax is brown or black in color. The pure bitumen when subjected to repeated distillations with superheated steam yields a refined montan wax which is yellow in color, lustrous, somewhat brittle, and has a melting point of 75°.

Purification of Montan Wax. Montan wax is purified and refined by treating it with a sulfuric purifying agent in a quantity amounting to at least one-quarter of the weight of the wax treated, thus separating the wax from the impurities present, according to Stickdorn.[24] The wax is melted to 100–150°; the acid is added while stirring the mass vigorously at a temperature preferably between 130–150°, until the desired purification is complete; this usually occurs in from 4 to 8 hours. The sulfuric acid purifying agent may be concentrated sulfuric acid, its monohydrate, fuming sulfuric, or chlorosulfonic acid, and acid compounds, such as alkali metal bisulfates. The treatment produces a paste-like material which is then washed with water, and subsequently neutralized with a small quantity of alkali metal bisulfates. The washed or neutralized wax is then dried, and may be further purified by solvent extraction. A light yellow colored wax may be obtained by distilling off the solvent. The light yellow montan wax has an acid value of 120 and a melting point of 80°.

For the production of *bleached montan wax,* Pungs and Jahrstorfer[18] suggest that the wax be first saponified and the resulting fatty acids and alcohol separated. The alcohols are bleached by a solid absorbent, such as activated carbon, and the acids are separately treated with an oxidizing solution—potassium dichromate and sulfuric acid. The bleached substances are then re-esterified, and by controlling the proportions of acids and alcohols used or by adding other alcohols or acids, the properties of the wax may be modified.

Properties of Montan Wax. Montan wax is soluble in benzene, chloroform, carbon tetrachloride, and hot petroleum benzine; insoluble in water; and incompletely soluble in hot ether or boiling alcohol. Refined montan wax has a melting point (Ubbelohde) between 80° and 86°; an acid value of 64–93, and a saponification value of 67–95. The wax contains esters of monohydric alcohols, and free alcohols and acids of high molecular weight, as the chief constituents. Montan wax cannot be distilled at ordinary atmospheric pressure without decomposition, but when distilled in a current of steam *in vacuo*, a white crystalline product results; *viz.*, montanic acid. The yield is said to be about 30 per cent.

Meyerheim[12] states that montan wax is found in brown coal in amounts from 1 to 27 per cent. It is obtained either by distilling it off with superheated steam or by extraction with benzene, carbon tetrachloride or trichloroethylene. The crude wax contains resinous and sulfur compounds and their esters together with wax alcohols. These acids amount to 50 per cent and melt at 82°. The constants of the crude wax are: dropping point 86°, acid value 25, ester value 53, saponification value 78, iodine number 17.6, unsaponifiable 36.4 per cent. Montan acids extracted with benzene give: drop point 64°, acid value 18.4, ester value 39.2, saponification value 57.6, iodine number 40, unsaponifiable 50 per cent. The constants of the distilled and refined wax average as follows: melting point 77°, acid value 82.7, ester value 7.6, saponification value 89, iodine number 10.9, montanic acid 62.6 per cent, unsaponifiable 37.3 per cent. *Montanic acid* melts at 84° and has the formula $C_{29}H_{58}O_2$ according to Hell and Boyen. Meyerheim refers to a mixture of *arachidic, lignoceric,* and *behenic* acids in the crude, and alcohols of 20 to 22 C atoms. These constituents are undoubtedly present.

In 1930 Holde isolated from montan wax *octacosanic acid* ($C_{28}H_{56}O_2$, m. 89°) using micro distillation methods, and this was confirmed as the normal acid by x-ray analysis. He isolated *hexacosanic acid,* m. 85.9°, from the mother liquor, which does not agree with the synthetic hexacosanic acid ($C_{26}H_{52}O_2$, m. 88.2°). *Behenic,* $C_{22}H_{44}O_2$ and *tetracosanic,* $C_{24}H_{48}O_2$ acids were also believed to be present. Holde believed that the acids derived from montan wax all contain an even number of C atoms and normal C chains. Holde's findings are not wholly in agreement with those of other investigators.

Pschorr and Pfaff[17] describe the crude wax from the Riebec Montan Works (Germany). The wax has an acid value 22.7, ester value 36.7, saponification value 59.4, and iodine number 13.9. They extracted the wax with ether obtaining 30.8–39.5 per cent extractibles, and subsequently with acetone which yielded 12.1–22.6 per cent, leaving a residue of 48.4–47.3 per cent. The ether extract contained free acids and the alcohol, *tetracosanol,* $C_{24}H_{50}O$. The acetone extract contained most of the free wax acids, and ceryl alcohol, free and combined. The residue was rich in esters, from which upon saponification three alcohols, *tetracosanol* m. 83°, *ceryl alcohol* m. 79°, and *myricyl alcohol* m. 88°, were isolated. The ether extract similarly yielded the alcohols, chiefly tetracosanol, and the acetone extract contained mostly ceryl alcohol. The calcium salts of the saponified extractions after acetone extraction, yielded on decomposition with hydrochloric acid, a crude *montanic acid* from which a pure ethyl ester m. 66.5°

was obtainable. This ester on hydrolysis gave an acid with molecular weight 426, and melting point 83.5° (m. wt. of $C_{28}H_{56}O_2$ is 424.7). The pure acid is easily obtainable from the acetone extract of the crude. Pschorr and Plaff[17] conclude that the crude montan wax contained 17 per cent of free crude montanic acid, and 53 per cent of esters of same, and a minimum of 30 per cent of substances of unknown composition. They found a fraction of 1 per cent of a resin, $C_{24}H_{34}O_2$, in the ether extract of the crude wax. This resin has a saponification value of 0, an iodine number of 54, and crystallizes in prisms melting at 241°.

Marcusson and Lederer[10] in 1932 had reported on the constituents and constants of two crude montan waxes as follows: resin 29, 29; brown coal dust 0.2, 0; alcohols 17, 6.7; normal wax acids 49.5, 52.3; hydroxy acids 3, 3; acids containing sulfur 6.5, 8; melting point 76–82°, 76–82°; acid value 27.8, 31.0; ester value 61, 61; saponification value 88.8, 92.

Lüdecke[6] has reported a melting point of 77–85° for crude montan wax with an acid value 28–36, and a saponification value 80–86. The refined montan wax melts at 83–84° and has an acid value 40–70, and a saponification value 62–75. It contains principally *montanic acid*, $C_{28}H_{56}O_2$, m. 86°. Brückner refers to the acid constituent as *geoceric acid*, $C_{29}H_{58}O_2$, which is undoubtedly synonymous with what has been also referred to by other investigators as *carboceric* or *montanic acid*, m. 86.6°, a branched chained isomer of *nonacosic acid*, m. 90.3°. He also mentions other constituents: *tetracosanol*, $C_{24}H_{49}OH$; *ceryl alcohol* $C_{26}H_{53}OH$; *myricyl alcohol*, $C_{30}H_{61}OH$; a ketone, $(C_{27}H_{55})_2CO$, m. 95.6°, known as *montanone*. The crude montan wax has been reported as containing almost two-thirds montanic acid and nearly one-third ketone. Pschorr and Pfaff,[17] and Grün and Ulbrich[5] favor the montanic acid as being an isomer of *octacosanic acid*. Possibly the wax contains both the C_{28} and the C_{29} acids.

Tropsch and Kreutzer[25] esterfied the crude montanic acid of montan wax with methanol and then distilled the ester at 5 mm pressure. A fraction boiling at 265–267.5° contained an acid $C_{27}H_{54}O_2$, m. 82°, crystallizing from ethyl acetate in clumps of needles, which appeared like a twig of fir under the microscope. It is apparently identical with an acid isolated by Gascard from Chinese insect wax, and is given the name *carboceric acid*. The fraction of the esters b_5 277.5–270° contains the true *montanic acid*, $C_{29}H_{58}O_2$ m. 86–86.5°.

In view of the findings of the various investigators it would appear as if there might well be three so-called montanic acids, and a preponderance of so-called C_{28} may be to some extent only a mixture of C_{27} and C_{29} acids. The situation here is not unlike that of cerotic acid.

Eisenreich[3] investigated a purified yellowish-white "mountain wax" (Montanwachs) of crystalline structure such as is used for candle making in Schliemann's factory at Hamburg. It had a melting point of 77°; acid value 93.0; saponification value 94.6; ester value 1.9; iodine number 12.0 (Wijs), acetyl acid number 93.0; unsaponifiable matter 29.07 per cent; acetyl number 11.8. A larger quantity of the montanic acid was purified by repeated crystallizations, producing a final crop of 40 grams of crystals of 82.5° melting point. This was precipitated in fractions from alcoholic solution by magnesium acetate, the different fractions showing melting points of 83°, 83°, 83°, 83°, 82.5° and 81.5°. Ultimate analyses of some of these fractions and quantitative determinations of some of their salts agree with the formula $C_{29}H_{58}O_2$ as established by Hell. The purified recrystallized unsaponifiable matter consisted of silky flakes which melted at 63.5° and gave negative results when tested for OH groups. The molecular weight by Beckmann's boiling point method gave the value 580, equivalent to $C_{42}H_{86}O$.

The following is the approximate composition of crude montan wax.

Esters of Wax Acids: 58–59 per cent
octacosyl esters of C_{20}, C_{22}, and C_{24} acids
octacosyl cerotate, m. 81°
octacosyl hydroxyoctacosanate, $C_{27}H_{54}(OH)CO \cdot O \cdot C_{28}H_{57}$, m. 93° (17–18%)
montanyl montanate (C_{29}, C_{29} ester), m. 89°
ceryl octacosanate, $C_{27}H_{55}CO \cdot O \cdot C_{26}H_{53}$ (m. 85°?)

Free Wax Acids: 17–19 per cent
carbocerotic acid, $C_{27}H_{54}O_2$, m. 82° (T & K)
montanic acid, $C_{29}H_{58}O_2$, m. 86.8° (T & K)
melissic acid, $C_{31}H_{62}O_2$ (T & K)

Free Monohydric Alcohols—Primary: 3–4 per cent
tetracosanol, m. 83° (P & P)
hexacosanol, m. 79° (P & P)

Secondary Alcohols: 1(?) per cent
$(C_{27}H_{55})_2CHOH$, montanol, m. 59–60° (G & U), 66°

Resins: 10–12 per cent
$C_{20}H_{30}O_2$, and neutral resins
$C_{24}H_{34}O_2$, montan resin, m. 241° (1%)

Ketones: less than 10 per cent
$(C_{27}H_{55})CO$, cerotone, m. 95°
$(C_{29}H_{59})CO$, montanone, m. 97°

The refined wax contains a much higher content of free wax acids and is substantially free from the esters of the C_{20}, C_{22}, and C_{24} acids.

Smelkus[23] found 4.5 per cent of an ester of a sulfur containing hydroxy-acid of a molecular weight of approximately 525 in montan wax crude. This might be associated with the acid $C_{31}H_{62}O_2$ found by Tropsch and Kreutzer[25] to the extent of 4.7 per cent of the total acids present in the crude after saponification.

The constants of steam distilled and sulfuric refined montan wax may be summarized as follows:

	Lewkowitsch	Graefe		Eisenreich	Marcusson & Smelkus
		a	*b*		
Melting point	80°	80°	77°	77°	74°
Acid value	123	102	71	93	65
Ester value	4	—	3	2	11
Saponification value	127	102	74	95	76
Iodine number	?	10	—	12	—
Unsaponifiable	7%	23%	46%	29%	50%

The mean values of the constants based upon these tabulated figures would be as follows: melting point 77.6°, acid value 91, ester value 5, saponification value 95, iodine number 11, unsaponifiable 31 per cent.

The chemical composition of this distilled and refined wax must be approximately as follows:

	%
Montanic acid	22–23
Hydroxymontanic acid	48–49
Montanyl alcohol	7– 8
Hydrocarbons (saturated and unsaturated), ketones	21–22
Total	100

Uses of Montan Wax. Montan wax has been of great importance in its industrial applications, that is for electrical insulation, for wax coatings on leather, for polishes, for brewer's pitch, for shoe pastes etc. Crude montan wax may be advantageously employed to lower or depress the pour point of oil. It has also furnished a base for the manufacture of synthetic waxes of high molecular weight, the acid constituent for esterification to the montanyl ester of montanic acid.

Peat Wax

Peat wax may be defined as the yellow waxy substance derived from peat by extraction with a suitable solvent. In 1907 Zaloziecke and Hausman,[27] by passing alcohol vapor through a tube filled with peat, noticed that the alcohol extracted a waxy substance from the peat, which is of a chrome-yellow color in its alcoholic solution and separates out in dark yellow flakes or powder on cooling, and these flakes melted at 80–96°. The waxy material was described as easily soluble in amyl alcohol, less soluble in ethyl alcohol and methyl alcohol and only partially soluble in ethyl ether and benzene, giving a dark green solution and leaving a brown residue. The crude wax was separated by selective extraction with ether into soluble and insoluble portions, which upon saponification with sodium hydroxide give two alcohols and two acids, indicating that these substances are esters of organic acids. The two alcohols seem to be identical; they are yellow in color and melt at 124–130°. They correspond to the formula $C_{20}H_{40}O_4$ with a molecular weight of 344. The brown substance insoluble in ether melts at above 260° and has the formula $C_{21}H_{35}O_7$, with a molecular weight 399. The acid of the substance soluble in ether is green in color, softens at 145°, and melts at 184°. It has the formula $C_{16}H_{25}O_5$ and a molecular weight of 297. There are also unidentified substances in peat wax.

Brown Coal Montana

There exist extensive deposits of brown coal in Bohemia, or Czechoslovakia, in the Ukraine, and in Russia proper. The best solvent for extracting the wax from Ukrainian brown coal is said to be a mixture of equal parts of crude alcohol and benzene. The wax extracted has a melting point of 84.6–89.0° and is similar to the German product.

Russian deposits have been extracted with dichloroethylene. The bitumen so obtained can be deresinified by dissolving it in two parts of benzene and precipitating the wax with four to eight parts of crude alcohol. The wax obtained melts at 80–86°. It can be bleached by subjecting it to a mixture of potassium bichromate, sulfuric and nitric acids at a temperature of 105–115° for seven hours; a pale yellow wax melting at 79–81° results. The yield is reported as 73 per cent.

In Ukraine three types of wax appear to be of economic importance, (a) *lignite wax* or bitumen (like the German crude montan wax), (b) *saprolite wax* from saprolite coal, (c) *peat wax* from low moors. Both (a) and (b) fuse readily with paraffin or ceresin, are black in color, and will polish to a high luster, thus making these waxes of value in the manufacturing of shoe-polishing materials in Soviet Russia. It is reported that the lignite wax has also been successfully bleached for use in the industries.

Peat Montana Wax

Ryan and Dillon[21] have referred to the montan wax obtained from Irish peat as *montana wax*. They describe it as a yellow crystalline wax melting at 76°, soluble in warm organic solvents; acid value 73.3; saponification value 73.9, and iodine number 16.0. The Irish montana wax contains 53 per cent saponifiable matter. The acid is montanic acid, $C_{28}H_{56}O_2$, the name being suggested by von Boyen. The acid has been prepared in its pure state, and melts at 83°, and has a mean acid value of 138.3. The unsaponifiable matter crystallizes out from benzene to fine needles m. 58–59°, density 0.92, and contains no appreciable amount of primary or secondary alcohols.

Ryan also refers to a *montanin wax* which seems to be a neutralized montana wax. This montanin melts at 95–97°. It is a white wax of hard texture, density$_{15°}$ 0.980, acid value 56.9, ester value 1.0, saponification value 57.9. It contains 41.3 per cent montanic acid, 23.9 per cent sodium montanate, and a remainder of unsaponifiable.

Any crude *peat wax* may be regarded as composed of (a) resinous, (b) waxy, and (c) asphaltic constituents. It is the latter (c) that renders the wax incompletely miscible with molten paraffin wax. It is only the (a) and (b) components that resemble those of montan wax. The amount of asphaltic (c) constituent varies greatly with the origin of the crude peat wax; it is fairly high in the wax from Chatham Islands, New Zealand.

The Chatham Island moorland covers 40,000 acres with an average thickness of 14 feet to the peat deposit. The peat will yield 9.4 per cent of a crude wax having a melting point of 73°. The size of the peat deposit and its high wax yield may serve to illustrate the importance of a future peat wax industry.

Lignite Montana Wax. A suitable substitute for the montan wax extracted from the lignites of Saxony and Thüringia is found in the dark, hard, and odorless ester wax extract from Devon lignite. It is of a higher melting point (80°) and harder texture than similar waxes extracted from the various English and Scottish peats.

Mona Wax. In 1926, Reilly[19] studied the thermal decomposition of Irish peat under reduced pressure. In the rapid distillation of dry peat in a vacuum Reilly (and Pyne) obtained less gaseous products and more tar, especially of the higher boiling point or more paraffinic fraction, than is the case in the distillation at the ordinary pressure. In 1930 Reilly (and Donnely) reported that the low-temperature distillation of peat comparable with that of various types of coal yielded: tar 16.64 per cent, phenols 5.4 per cent, acetic acid 22.6 pounds, ammonium sulfate 17.4 pounds, and 8.6 per cent of gas. Later Reilly (and O'Sullivan) mixed pulverized peat with one ninth of its weight of chalk, and distilled the mixture at 550° in an electrically heated retort. The chalk however did not change the yield in tar nor its character. They were able to show through a careful study that the tar produced is a function of the wax content of the peat. By extracting the wax portion from the peat and subjecting it to distillation the products obtained, that is extractables with selective solvents—ether, alcohol, and acetone in this order—are not particularly different from those of the wax-free peat. They concluded that over 40 per cent of the tar produced is derived from the 10 per cent of wax in the powdered black peat.

The studies referred to are still being carried on. In 1931, Reilly reported that successful results could be obtained in the extraction of wax from Highland peat by using certain mixtures of solvents such as petroleum spirits with alcohols (methyl, ethyl, isopropyl, or propyl); that is, azeotrope-like mixtures that can be recovered without interference from the wax or water in the solvent mixtures. In 1940 Reilly (and Emyln) reported that a sample of peat which gave 8.4 per cent crude wax with petroleum spirit, on extraction with a mixture of the same petroleum spirit mixed with isopropyl alcohol (70 : 30), yielded 10.6 per cent of extract. Of this 10.6, 2 per cent was readily extracted by cold alcohol, yielding mainly resinous matter; the remaining 8.6 per cent was similar to crude wax obtained by petroleum spirit alone. The presence of moisture does not hinder the removal of the wax by petroleum hydrocarbons. Crude wax from peat, which may contain bituminous matter in considerable amount as well as non-polar resins, has been named *mona wax*. It is softer than montan wax, and 10 to 15 degrees lower in melting point, of a slightly higher dielectric strength and a slightly lower solvent-retention power.

Protoparaffin and Pyroparaffin. Marcusson[9] theorized as to the difference in the paraffins as they exist in crude oil and in the distilled oil from brown coal. He referred to the crude oil paraffin as "protoparaffin" and the distilled oil paraffin as "pyroparaffin." The "protoparaffin" has a higher molecular weight, greater hardness, higher density and is of a more wax-like consistency. It is an isoparaffin and changes to normal paraffin upon distillation. By prolonged heating of montan crude the saponifiable matter almost disappears from the soft waxy product, the oil content being increased at the expense of the solid matter. In the destructive distillation of montan wax most of the hydrocarbons are formed directly from the esters, rather from the ketones. By heating crude montan wax in the presence of kieselguhr as a catalyzer, and then treating with concentrated sulfuric acid, mixing it with fuller's earth, and extracting with benzene, Marcusson found that he could secure a wax of 64–66° melting point identical in appearance to ozocerite ceresin.

Ceresin

The word *ceresin* is derived from the Latin words *cera*, meaning "wax" (beeswax), and *sine* meaning "without," or "free from." That is, *ceresin* is a material "free from wax" (beeswax). The Spanish words are *cera* and *sin* respectively, and have the identical meaning, hence the word *cerasin*. Ceresine, spelt with a final "e," is a name sometimes applied to an imitation of the so-called genuine ceresin.

Ellis[4] defined ceresin as a "purified form of ozocerite, which presumably consists also of a mixture of paraffin hydrocarbons, probably isoparaffins, of somewhat higher average molecular weight than those of paraffin wax." In discussing the wax bearing distillates Ellis said "the solid hydrocarbons called *ceresin* display both chemical and physical properties quite different from paraffin wax. In contrast to paraffins, ceresins retain oil very tenaciously and cannot be separated therefrom by the usual process of filtering and pressing. At similar melting points, the ceresins have a much higher lecular weight, specific gravity, viscosity, boiling point and nitrobenzene ints than paraffins. They have a very delicate crystalline structure, the crystals being of fine needle or short plate type. Chemically the ceresins are much less stable than solid paraffins and react readily with fuming sulfuric or with chlorosulfonic acid, a fact which has been interpreted to indicate an isoparaffinic structure." The broader use of the term as used by Ellis to define ceresin by its composition rather than its source, means that ceresin may arise from wax bearing distillates of any kind, whether natural mineral (ozocerite), petroleum refining (*petroleum ceresin*), or lignite refining (*cerasin*).

Although ozocerite is the original source of ceresin, it has competed keenly with a similar isoparaffin product (cerasin) produced by a low temperature distillation process at Saxony and Thüringia, in which a wax recovered from detarred lignite is fused with semi-refined ozocerite, and the whole then bleached white. Factories in Meisel, near Darmstadt, and in Hamburg, are said to have produced various grades of *cerasin*, some of which contained bleached montan wax and at least twenty per cent of imported paraffin.

LIGNITE PARAFFINS

German Brown Coal Paraffin

Paraffin is obtained by destructive distillation of German brown coal. The wax-bearing distillates are refrigerated, admixed with a diluent, filtered, and the slack wax thus obtained is sweated out to remove the entrained oil; the refined paraffin wax has an average composition of $C_{26}H_{54}$. In the sweating and pressing operations the paraffin is separated from the paraffin oils by introducing into the mixture certain disc-formed cooling elements, from which the separated paraffin is continuously removed by scraping the stirring device to secure the greatest possible cooling action. This method was taught by Porges and Neumann,[16] and is used today in principle by American refiners of petroleum paraffins.

It is reported that a specimen of the brown coal paraffin contained no more than 10 per cent of isoparaffins possessing the mean formula $C_{22}H_{46}$. Naphthenic hydrocarbons C_nH_{2n+1}, C_nH_{2n}, C_nH_{2n-2}, and C_nH_{2n-3} have been found in waxes melting at 76°, 63°, 57°, and 50° respectively.

Lignite Paraffins

The English, Rhenish, Westphalian, and particularly "Oedingian leaf" shales yield paraffins. "Bituminous shales" in Sicily, Sweden, Esthonia, and Serbia yield burning, intermediate, and lubricating oils, and a considerable amount of "paraffin scale," both hard and soft.

Bituminous lignite has been used for many years as a material for the dry-distillation process, and the working up of the resultant lignite tar into mineral oils and paraffin, particularly in the Saxony-Thüringian district. The distillation of lignite tar is conducted at about 650° in a manner best suited to separating oil as free as possible from paraffin, and concentrating the paraffin in the paraffin masses.[22] To do this, the chemically treated crude oil is distilled into one or two oil fractions and a paraffin mass, and the separation of the oil and mass takes place as soon as the distillate is congealed by refrigeration. The first oil distilled contains the lighter ends such as lignite-tar benzine, solar oil, and pale heavy oil, as well as the solar paraffin mass. The latter on pressing yields "solar-paraffin scale" and a gas oil which is marketable. The principal paraffin mass of the tar yields another "paraffin A-scale" and the filter oil which on distillation, not to dryness, yields crude oil and paraffin mass B from which on distillation is obtained filter oil and "B-scale." B-scale is distilled to red oil and paraffin mass C and which can be worked up into "filter oil heavy" and "C-scale." A-scale is the hard paraffin mass, and B and C are the softer masses, which are also crystallized out at a lower temperature. These paraffin masses are worked up to furnish the *refined paraffins* much in the same way as some petroleum paraffins are handled. There are, of course, many possible variations in the process described above.

The following are melting points of crude paraffins or scale waxes: "A-mass" 50–55°, "B-mass" 40–45°, "C-mass" 38–42°, "solar-mass" 35–40°. In the refining, the paraffin masses are first crushed in a mechanical crusher; the pulpy mass is drawn by a pump and delivered to the filter press, where the crystals of paraffin are separated from the oil. The filter press is of the filter plate type. The paraffin cakes are scraped from the cloths of the plates with wooden knives. The press cake contains oil and.is hence transferred to a vertical press and subjected to a pressure of 100 or 150 atmospheres to press out the oil. The press cake is subjected to further treatment with crude benzine and direct steam heat in the melting vessel. When the mixture of wax and benzine is poured into water the paraffin solidifies. Then when the scale is pressed in a hydraulic press, the benzine, which is a lignite-tar distillate, carries away with it the heavy oil adhering to the scale. To refine the paraffin the process is repeated twice; that is the scale receives two pressings. Scottish paraffin, however, has a more crystalline structure than that of the Saxony-Thüringian, and is recovered admirably by sweating, requiring no benzine washing.

Refined paraffin that has been washed as described would still contain traces of benzine. The paraffin to be fully refined must be placed in a retort or cylindrical vessel, warmed by means of steam, and the benzine swept out by the action of a steam jet placed under the vessel. After the paraffin has been rendered inodorous by steaming, it is still faintly greenish yellow in color—not pure white— and must be treated with decolorizing agents such as animal charcoal, ferrocyanide residues, clay, or a mixture of pure carbon and silicate, preferably the latter. The decolorizing agent must be anhydrous, or made so; 1 to 2 per cent of the dry powder is added to the melted paraffin, and mechnically mixed in the vessel which is heated to 70–80° by steam. The filtering can be done through paper, and with the same type of equipment used in pressing petroleum paraffin.

In crystallizing lignite paraffin, cooling is effected in shallow vessels by means of air, but the soft masses are further cooled with refrigerating brine in a manner similar to the handling of petroleum paraffins.

The grades of refined lignite paraffin range in melting point from 35° to 62°. Grades melting below 50° are classed as *soft paraffin,* and those of higher melting point as *hard paraffin.* Paraffin from lignite ignites at 160–165° and volatilizes at 350–400°. The density of lignite paraffin rises with the rise in melting point; *e.g.*, 0.883 for paraffin m. 45°, 0.908 for that m. 51°, and 0.915 for that m. 58°, the densities being determined at 20°. The specific heat of lignite paraffin is 0.683.

Lignite paraffin scale, m. 35–40° (95–104° F) is used mainly in the manufacture of matches; that is, for impregnating match sticks. According to Egan and Mills[2] paraffin scale can be mixed with split fatty acid of a hydrogenated oil to an iodine number of 5 or less, in making candle material.

Lignite tar distillates are obtainable from many sources of bituminous lignites and shales found all over the world. Some are richer in wax than others. In the United States there is a black lignite in the state of Washington that has been found to produce 108 pounds of tar per ton. The tar on redistillation gave approximately 26 parts of light oil, 29 parts of middle oil, 7 parts of *paraffin,* 39 parts of heavy oil, and 4400 cu ft of gas, and the coke left in the still. The tars of French and Scotch shales are also reported to yield a considerable amount of wax.

Surakhansk Ceresin of Russia. Surakhansk ceresin when fully refined has a density of 0.788 at 99°/20°; solidification point of 87.7° (190° F), and a molecular weight of 625.5 calculated for $C_{45}H_{92}$, 632.7. It is a mixture of isoparaffins, consisting chiefly of $C_{45}H_{92}$ and some $C_{22}H_{46}$. It is to be noted that Surakhansk ceresin is one of the highest melting point hydrocarbon waxes known.

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Chapter 5

Petroleum Waxes

Classification of Petroleum Waxes

It is difficult to draw up a classification of petroleum waxes that could not be subjected to criticism. The classification given here is somewhat different from others that have been proposed.

(1) Paraffin Wax Group
    Softer paraffins (*e.g.*, slack wax)
    Intermediate paraffins (*e.g.*, scale wax)
    Harder paraffins (*e.g.*, block waxes)
(2) Petrolatum Group
    Petrolatum (petroleum jelly)
    Petrolatum wax (high penetration)
(3) Petroleum Ceresin Group[2]
    Microcrystalline wax (low penetration)

In fractionating crude petroleum the fraction or cut known as *paraffin distillate,* boiling from 170° to 310° when distilled at a very low pressure, can be separated into solid wax and liquid oil fractions by chilling and filter-pressing. The solid fraction which contains 65 per cent wax is the *slack wax* which is sweated and refined to the regular paraffin of commerce (see refined paraffin wax, p. 000).

The softer paraffins include *slack wax* and *sweat wax,* the latter a more oily by-product of the former (see softer paraffins, p. 000). The intermediate paraffins include the *yellow scale waxes* and *white scale wax,* which are derived by sweating out the greater part of the oil from slack wax. When scale wax is subjected to further sweating to remove the oil and the resultant paraffin is bleached, it becomes a *refined paraffin* or *block wax.*

After the paraffin distillate is fractionated from the crude petroleum, a higher boiling cut, known as the *high viscosity fraction,* is distilled. This fraction also contains wax, but because of its microcrystalline nature does not lend itself well to separation by filter-pressing. The high-viscosity fraction is cold settled and centrifuged, thus yielding an oily wax portion, known as *petrolatum stock,* and oil. Petrolatum can be refined from the petrolatum stock, or the *microcrystalline wax* in the petrolatum stock can be separated by recrystallizations and settlings from naphtha solution at reduced temperatures (see microcrystalline wax, p. 240).

PARAFFIN WAXES

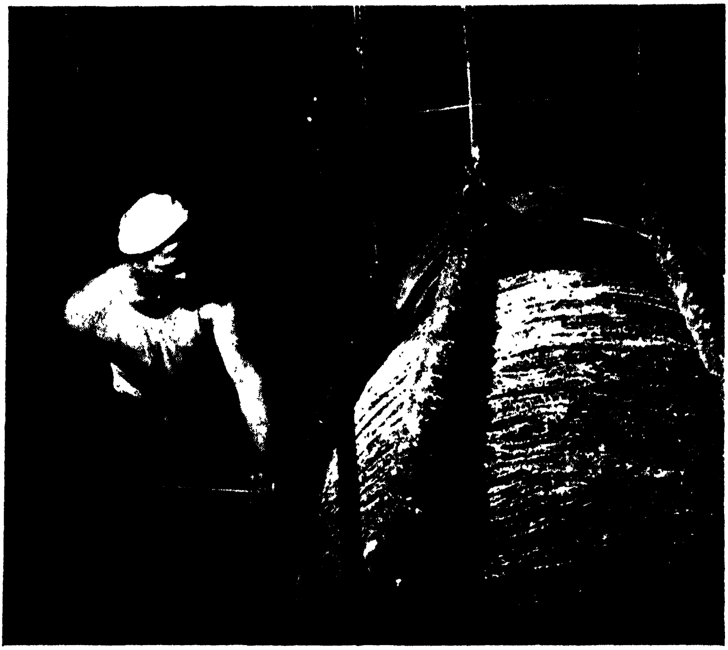
Scale Wax

Scale wax is the paraffin that is derived by a process of sweating the greater part of the oil from slack wax. It contains up to 6 per cent of oil. The most important grade is the *white scale wax* which has a melting point of 124°–126° F and contains 2 to 3 per cent of oil. A special *refined white scale wax* for crayon manufacture and other uses is made by a "second pudging and pressing," and contains less than 1 per cent of oil. Scale waxes contain paraffin oil when they are subjected to the final washing, pressing, and bleaching in their conversion to block paraffins. The scale waxes are used industrially where penetration of paraffin is desirable. Scale waxes are more translucent than block paraffins, and are crumbly solids at low temperatures. They are not entirely stable in color even when bleached, nor are they free from taste and odor. Crude scale paraffins are yellow. Yellow scale paraffins are produced in high as well as low melting points, but the softening points are always low.

Refined Paraffin Wax

Refined paraffin wax is commonly designated as "paraffin wax" or simply "paraffin." The word "paraffin" appears to be a French derivative of the Latin *parum*, meaning "little," and *affinis*, meaning "affinity"; in other words, a chemically inactive substance. Paraffin was the name given to the wax-like substance derived from the distillation of wood. *Refined paraffin wax*, or block paraffin, is a hard crystalline hydrocarbon wax derived from mineral oils of the mixed base or paraffin base type by a process of refining, in which the oil is eliminated or reduced to a negligible extent. The setting points of paraffin wax range from about 90° to 160° F (32.2° to 60°). The flash point of paraffin wax is over 350° F (177°). The United States Pharmacopœia defines *paraffin* as a derivative of petroleum, whereas the British Pharmacopœia defines it as a product derived from the distillation of shale. Its specific heat approximates 0.694.

In the refinery the crude oil is subjected to distillation whereby a *paraffin distillate* is separated. The paraffin distillate is chilled to a low temperature, between 0 and 35° F, and the solid wax filtered from the oil. The resultant slack wax is subjected to a *sweating* operation, usually after redistilling. The wax may be further refined by sulfuric acid, percolation through clay, or other means. The resultant paraffin wax is graded according to its tensile strength, melting point, oil content and hardness.



Courtesy Standard Oil Co. (N. J.)

FIGURE 12. Workman opens the plates of one of the battery of big hydraulic presses which squeeze wax from the chilled distillate as the first step in production.

Courtesy Standard Oil Co. (N. J.)

FIGURE 13. Solid wax is chipped from the canvas face of one of the filter plates. It will be refined by sweating, chemical treatment, and filtering.

The paraffin distillate is pumped through a bank of cooling units, consisting of a series of pipe coils placed in a steel jacket of circulating liquid ammonia. It is then pumped to hydraulic presses in which are locked hundreds of canvas covered circular metal plates (Figures 12 and 13). For a description of sweating out the wax and its further refinement, see pp. 221 and 222.

Source of Paraffins

Crude petroleums are essentially hydrocarbons, since they usually contain more than 97 per cent of hydrocarbons having a carbon content of 83-87 per cent, and a hydrogen content of 11–14 per cent; the remaining elements are oxygen, nitrogen, and sulfur.

The crudes differ from each other chiefly in the proportions they contain of the various hydrocarbon series, *i.e.*, paraffinic, aromatic, asphaltic, and naphthenic. For example, Pennsylvania crude is a good example of a crude petroleum with a paraffinic base, which on steam distillation will yield a cylinder stock from which paraffin wax can be directly recovered. California crude is of a naphthenic base and contains a fair amount of aromatics, but little or no wax. Tampico crude has an asphaltic base, and certain Russian and Gulf Coast crudes, a naphthenic base. Although a crude such as Pennsylvania may be made up almost entirely of normal straight chain series, on distillation the hydrocarbons may change appreciably to isomeric paraffinic, olefinic, and naphthenic; the latter is like olefinic but in closed chain formation. The solid or waxy portions, according to Mabery,[16] tend to retain the C_nH_{2n+2} structure.

The modern classification of petroleum hydrocarbons calls for the following groups: paraffinic, aromatic, naphthenic, polyaromatic (cyclic), polynaphthenic, and asphaltic, all of which more or less blend into each other. A petroleum may be a fairly well balanced mixture of two groups, such as paraffinic and naphthenic, it is then referred to as paraffinic-naphthenic, *e.g.*, Ssurakhanui, Baku crude.

Paraffin wax occurs naturally in many crudes, associated with paraffin oils. Pennsylvania and Mid-Continent oils contain a high percentage of paraffin wax; California oils are almost wax-free. Gulf Coast oils, however, vary from naphthenic oils with almost no wax to oils such as Rodessa which contain even more wax than the Pennsylvania crudes. Differences in the physical characteristics of the paraffin waxes can often be ascribed to the origin of the crude.

Recovery of Paraffin Wax

When Pennsylvania crude petroleum, or other paraffin yielding petroleum, is distilled destructively in a cylindrical still, the primary distillation is carried out in five steps. The first cut yields light naphtha, the second heavy naphtha, the third high test burning oil, the fourth low test burning oil, and the fifth portion is the undistilled residuum or tar, which is the source of paraffin wax. This residuum is pumped to the *tar still,* which holds about 250 barrels, and is reheated to the point where the refinement was stopped in the cylindrical still, to a temperature at which it will again give off the desired vapors. A less expensive process requires the use of a continuous tower still which yields a wider range of products in the same run, and has a much lower cost of maintenance. With a tower still it is not necessary to pump the residuum to a separate tar still.

Irrespective of whether a tar or tower still is used, the residuum is distilled by increasing the temperature; a *heavy distillate* is taken off at the first trap, an *intermediate distillate* at the second trap, and a *light distillate* at the third trap, while *tar coke* remains in the still.

The first distillate is *wax bearing*, and in the last part of the run is known as *wax tailings.* The third distillate is a high-test oil, such as 300° oil; the second distillate is of intermediate character. About 5 per cent by weight of the crude remains in the still as coke which can be sold to industries as pure carbon. The *wax bearing distillate* is treated with 4 to 5 per cent of sulfuric acid, washed with water and caustic soda; the mixture is kept liquid by means of steam coils. After settling, the paraffin oil goes to the "chill rooms," where chilling is effected by pumping the distillate through tubes jacketed by cold brine and provided with helical scrapers. The resultant crystal mush is subjected to powerful pressure by plate and frame filter presses set in refrigerated rooms, and the refined heavy oil which drains off from the press is collected as lubricating oil. Its specific gravity should be about 32° Bé. The press cake may be broken up, melted, allowed to solidify, and then submitted to still greater pressure at a higher temperature (70° F) than before, when the product is known as *refined wax.* To convert it into the block paraffin it is washed with petroleum benzine, pressed, melted, filtered through bone black or other medium, and solidified into a hard, translucent, colorless block, referred to commercially as *fully refined paraffin.*

The yield of paraffin wax from American petroleum is 2 to 3 per cent, whereas the yield from Burmese petroleum is 6 per cent. Canadian petroleum yields less than 3 per cent. Much of the Russian petroleum contains no paraffin wax. However some of the Russian petroleum districts have waxy crudes, called "mazouts."

Russian Paraffin. The first paraffin plant built in Russia was in 1928, at Grozny, in the Northeast Caucasus, and consisted of two series of shell stills with four dephlegmators each. Grozny waxy crude is preheated by the bottoms from the last still, enters the first still, where its temperature is again raised, is then pumped to the following stills, and successive fractions collected to form the "semi-paraffin" stock. This stock is sent through a second series of stills where it undergoes the same treatment. The oil so obtained is easily worked in the paraffin presses at lower temperatures than those normally used. The sweating operation is improved, resulting in a wax of better quality than is ordinarily produced following a single distillation. A total of 40 to 45 per cent of wax distillate is recovered from the crude.

Paraffins from Grozny paraffin-base oil are reported as having melting points varying from 28.3° to 71.3°, and elementary compositions corresponding to $C_{19}H_{40}$ and $C_{35}H_{72}$ respectively.

Sweating of Slack Wax

Low-melting paraffin waxes are more soluble in oil than the high-melting waxes. Mixtures of high- and low-melting waxes have solubilities between those of the components. The solubility of paraffin wax in oil increases very markedly at temperatures 10 degrees below the melting point of the wax. In the refining of paraffin wax, the wax retains approximately 2 per cent of the oil at room temperature; but the amount retained at the temperature at which final sweating is carried out is too small to be detected. The presence of this small amount of oil in solution offers an exeplanation for some of the difficulties encountered in the separation of oil from wax.

The greatest loss in wax in the sweating process occurs at the temperature at which most of the oil is removed. Paraffin waxes are mixtures of lower and higher melting components which form solid solutions. Francis found that a mixture of two pure fractions of wax melted at a temperature lower than the melting point of either component. Myers and Stegeman[20] fractionated paraffin wax of 55° melting point *in vacuo*, and summed up the results of nine fractionations. Their results differed from those of Francis; they found that the freezing point of the solid solution lay between that of its components.

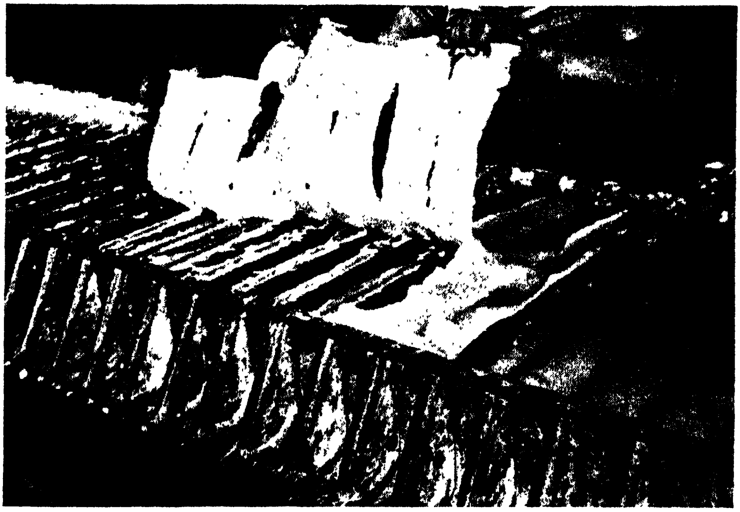
A wax distillate containing 80 per cent of oil and 20 per cent of wax is distilled over at 315° to 425° (600° to 800° F). This distillate is chilled and pressed to give: *slack wax* containing somewhat less than 50 per cent of oil and more than 50 per cent of wax; *spindle oils* with pour point of plus 6° to 7° (20° F). The slack wax is chilled and sweated to form *scale wax* which contains 1 to 6 per cent of oil, 99 to 94 per cent of wax, and *foots oil,* made up of lower melting point wax plus oil. The scale wax is then refined to paraffin waxes of different melting points, leaving a *slop oil* of little or no value. The refinement of higher melting waxes, with small loss in wax value, is achieved by washing the slack wax with a selective solvent; that is, one which is highly solvent for the oil and of low solvency for the wax, such as a mixture of benzol and methylethyl ketone. The solvent can be recovered from the foots oil without loss.

Production of Paraffin Wax at the Refinery

The following process and equipment has been prescribed for the refining of block paraffin from an Eastern Texas crude wax distillate. Basically the sweating process follows the Henderson modification of the early

Courtesy Standard Oil Co. (N. J.)

FIGURE 14. Liquid paraffin, fully refined, pours into one of the brine-cooled molds from which it is removed in slab form for shipment. An extra portion is released into the mold to allow for the shrinkage after cooling.



Courtesy Standard Oil Co. (N. J.)

FIGURE 15. As wax cools, surplus is stripped from top of mold. This overflow provides for shrinkage, insures uniform size and weight of slabs.

methods of Price's Candle Company. The slack wax from the chill room is melted and pumped to the pans in the *sweater house.* In this house are frames on each of which are set nine shallow long trays or pans one above another. The pans have a false perforated bottom with wire gauze held in the frame. The 2 inch space between the bottom and the gauze is filled with circulating cold water, and the melted wax is run on to the surface where it congeals to a sheet of about 4 inches thickness. After solidification the pans are tilted and the water is run off. The house has steam coils along the walls and under the pans for controlling the interior air temperature, and is equipped with vertical ducts between the frames to allow for air circulation. By a thermostatic regulator the temperature is raised 1 or 2 degrees F per hour, and the oil and soft wax that sweats out is drained off from time to time. The first running, or *light foots oil,* is used as a plant fuel, but the next, or *heavy foots oil* fraction, is pumped back to the wax distillate, and subsequent fractions are resweated, or used later for blending before the acid treatment. The end product is a block wax of 130/132° F melting point which still requires a finishing treatment to remove color.

Therefore the wax is melted and run into agitators (lead-lined and steam-jacketed), treated with strong sulfuric acid, violently agitated for 30 minutes, and settled for an hour. The acid sludge is then drawn off and the melted wax is run into another agitator, in which it is washed with hot water and then with sodium hydroxide and finally with a hot water spray. After removing traces of water by long settling, the wax is dried finally by blowing air through it.

The melted wax at this stage is not entirely colorless, and hence is run through vertical filters of hot fuller's earth. The filtered bleached refined wax is run into a slab mold, 40 ft or more in length, which consists of a tank like structure having a sealed bottom, open top, and a large size turn screw at one end. In this housing is a series of compartments formed by *chill plates*; each plate is filled with chilled brine and connected to the other with a flexible hose, so as to provide a continuous circulation. The plates are about 2 inches thick and spaced 1½ inches apart. The mold is filled with melted wax and the wax seeks its level by filling each compartment. After the wax is congealed, the screw at the end of the mold is unturned to loosen the plates; the plates are manually pried apart sufficiently to lift out the slabs of wax. These slabs constitute the *fully refined paraffin* of commerce. They are 12 in × 18 in × 1½ in in size, weigh about 10 pounds each, and are packed in bags stamped with the A.M.P. melting point. The paraffin is also packed loose and shipped in paper-lined freight cars.

U. S. P. Paraffin

The Pharmacopœia of the United States of America[23] defines paraffin as "a purified mixture of solid hydrocarbons obtained from petroleum." It describes paraffin as "a colorless, or white, more or less transparent mass, frequently showing a crystalline structure. It is without odor or taste, and is slightly greasy to the touch. Paraffin is insoluble in water and in alcohol; slightly soluble in dehydrated alcohol; freely soluble in chloroform, in ether, in benzene, in petroleum benzine, in carbon disulfide, in volatile oils, and in most fixed oils." Included in the "Tests for identity and purity" are the following. Specific gravity is given as "about 0.900 at 25°." "It melts between 50 and 57° [method of melting point minutely described]. When strongly heated Paraffin ignites, burns with a luminous flame, and deposits carbon." "Shake melted Paraffin with an equal volume of hot alcohol; the separated alcohol does not redden moistened blue litmus paper (acids)."

The British Pharmacopœia also describes paraffin as "colorless, semi-transparent, crystalline, inodorous and tasteless, slightly greasy to the touch. Specific gravity 0.82 to 0.94. . . . It melts at 130° to 135° F (54.40 to 57.2°) and burns with a bright flame, leaving no residue."

Paraffin wax crystals may be plate, needle, or malcrystalline. The crystals from a solvent are different from those of the melt. The mal crystal forms as an orientation of plate and needle.

Physical tests on paraffins are as follows: (1) Tensile strength, or the force necessary to pull the wax apart; (2) durometer hardness, or the maximum force which may be applied to a small plunger in a wax cake without forcing it in further; (3) consistency, or force necessary to push a plunger into wax at a uniform rate, which is akin to viscosity; and (4) flexibility, as determined by a bending test which measures force necessary to bend a plate of wax, and the angle to which it may be bent without cracking.

The tensile strength of paraffin waxes ranges from 60 to 120 pounds per square inch; most of the commercial paraffin waxes have a tensile strength of 180 to 210 pounds per square inch.

Range of Hydrocarbons in Paraffins

The first compound in the normal paraffin series that is solid at room temperature (68° F) is *n-heptadecane* melting at 22° (71.6° F). Slack wax contains hydrocarbons from *n-heptadecane* ($C_{17}H_{36}$) upwards. In fully refined paraffin wax (128–130° F m. p.) there is apparently no hydrocarbon (excluding traces of oil) below $C_{23}H_{48}$; the latter melts at 48° (118.4° F). Mabery[16] in 1902 isolated six fractions in a fully refined paraffin and these ranged from $C_{23}H_{48}$ to $C_{29}H_{60}$. However Buchler and Graves[3] isolated hydrocarbons ranging from C_{18} to C_{32} in a paraffin (from Wyoming distillates) that perhaps was not as close a cut as that of Mabery.

Mabery examined the paraffins of a *rod wax*, settled out of Pennsylvania crude oil and collected in the well pumping equipment. He found hydrocarbons extending up to $C_{35}H_{72}$, melting at 76 to 77°. Buchler and

Graves found C_{35} to C_{41} hydrocarbons in a Wyoming crude oil rod wax from sucker rods (see p. 247).

Krafft[15a] prepared synthetic paraffins and made a similar investigation of a lignite paraffin, hard paraffin, m. 80°, from Saxon brown coal; by means of distilling in the vacuum of a cathode light he obtained 35 fractions melting up to 93° and of indicated composition ranging from $C_{15}H_{32}$ to $C_{50}H_{102}$. Francis, Watkins, and Wallington[9] distilled a Scotch shale paraffin, m. 55°, very carefully in *vacuo*, and were able to secure seven well defined fractions of constant boiling point. The boiling points ranged from 150° to 219° at 0.05 mm pressure; melting points from 44.9° to 66.6°; molecular weight from 325 to 434; density at 100°/4°, from 0.7453 to 0.7678; solubility in chloroform at 15°, from 20.6 to 0.66; iodine number from 3.1 to 1.4. The $C_{32}H_{66}$ and the $C_{31}H_{64}$ hydrocarbons did not match *n-dotriacontane* and *n-hentriacontane*, and were evidently branched-chain hydrocarbons. Carpenter,[4] had found in wax from Burma crude, hydrocarbons from C_{21} to C_{34}, in which isomers of different melting points were noted from the same molecular weight. In rod wax of this same crude, a hydrocarbon $C_{57}H_{116}$, m. 96.5°, was recognized.

Marcusson[19] attempted to show that the protoparaffins left in undistilled petroleum wax are branched-chain hydrocarbons by converting the paraffins to aliphatic acids with oxygen in the presence of manganese dioxide or fuller's earth. He treated 20 grams of petroleum ceresin, m. 62 to 71°, with oxygen in the presence of manganese dioxide deposited on fuller's earth, at 125° for 35 hours, then for 55 hours at 150°. The resultant soft material was separated into saponifiable and unsaponifiable parts by the method of Höning and Spitz, giving 44 per cent of unsaponifiable. The latter portion had an iodine number of 8.5, and acetyl value of 21.0. The acids were separated by Varrentrap's method, giving oily acids and solid acids. The oily acids contained no hydroxy acids and had an iodine number of 11, acid number of 115, and density of less than 1; they were considered polymerized unsaturated acids. The solid acids had a melting point of 60 to 62°, a molecular weight of 384 and an acid number of 146; they were extremely soluble in the ordinary organic solvents, which is typical of branched-chain acids. Marcusson concluded that branched-chain hydrocarbons are present in ceresin or protoparaffin.

Hydrocarbons of as high a molecular weight as that of $C_{70}H_{142}$, heptacontane, m. 105.5°, have been properly identified; those of still higher molecular weight have been synthesized.

Residual Oil Content in Refined Paraffins

For certain uses it is important that the refined paraffin be free or almost free from oil. *Parawax* is a refined paraffin on the market that is free or almost free from residual oil, which makes it suitable for laundry and other household purposes, including the sealing of jams and jellies to prevent deterioration. For the latter process the melted refined wax is poured on the surface to form a cake of about ⅛ inch thickness. In cases where the wax is used in a solvent, as in the protection of valuable prints, Parawax is apt to leave a trace of residual oil, and the author finds that Asiatic petroleum wax of 135° to 137° F melting point answers the purpose more satisfactorily.

Asiatic paraffin wax imported from Burma and Sumatra contains but 0.02 per cent of oil. A comparison of the various types of paraffin is given below:

Grade of Paraffin	Per Cent of Residual Oil
White scale	2.40–2.70
Refined 122° F (A.M.P.)	0.25–0.28
Refined 125° F (A.M.P.)	0.16–0.17
Refined 130° F (A.M.P.)	0.08–0.09
Parawax	0.16
Asiatic 135/137° F (A.M.P.)	0.02

In the microcrystalline waxes, petrolatum wax of the softer grades contains 6–13 per cent of occluded oil, and the refined hard grades contain 1 to 5 per cent. The oil is of high pour point and is of such a nature that in technical use it will not separate at all. If any greasiness is noted it can generally be attributed to some residuum of the extracting solvents.

The oil in paraffin can be determined by any one of several methods:

(1) By hydraulic pressing of the wax specimen, 15 to 35 grams in size, and absorbing the expressed oil by blotting paper.

(2) By Holde or other solvent extraction, in which the residue, after evaporation of the solvent, is weighed. This method is said to give a 3 to 4 per cent error because the residue contains a little low-melting paraffin.

(3) By Wilson and Wilkin[31] refractive index determination of the residue. This method uses a petroleum solvent which has the same index of refraction as paraffin of 111° F melting point. A plotted straight line curve is used to read off the percentage of oil. The solvent consists of 45 per cent of Government mineral seal and 55 per cent of ligature oil and the determination is made at 77° F (25°).

These methods are not suited to microcrystalline wax. Wax of this type is taken up with hot ethylene dichloride and then chilled to 0° F to separate it from impurities. Evaporation of the solute yields the oil as a residue.

The effect of the presence of a small amount of oil in paraffin wax on the resultant tensile strength has been tabulated by Adams and MacLaren.[1]

The oil-free paraffin wax was crystallized from organic solvents such as acetone and benzol.

	Percentage of Oil Added	Tensile Strength (lbs/sq inch)
Oil-free paraffin m.p. 130° F	0.000	395
	0.020	300
	0.038	295
	0.154	160
	0.300	70
Oil-free paraffin m.p. 136° F	0.000	390
	0.004	387
	0.008	347
	0.034	324
	0.068	270
	0.136	244
	0.272	176
	0.544	115

Separating Waxes from Lubricating Oils

It was customary in the past to separate wax from oils (by operations involving settling, centrifuging, or filtering), using large filters, and spraying the wax cake on the filter with a solvent in an attempt to remove the oil. This scheme of operation, for example, is applied to the separation of the body of diluted oil from wax in the dewaxing of petroleum lubricating oils to produce low pour point lubricants.

According to Dons and Mauro[7] the separation of the wax from the oil can be more effectively accomplished, by (1) precipitating the wax in a cooled dewaxing solution; (2) extracting the main body of relatively free oil solution from the coalesced wax crystals; (3) subjecting the wax to forcible disintegration and deoiling operations so that previously trapped solution is removed from the wax.

The new system brings about simple cleaning action. A stream of wax clusters and oil solution is discharged into a settling zone, where the clusters readily separate and then pass into a distintegrating zone associated with a deoiling zone where each minute wax particle is forcibly cleansed by a counter-flowing solvent stream. The solvent or solvent blend selected should be an excellent oil solvent, but poor wax solvent and one which will retain a low viscosity even when containing much oil in solution. Good solvents for the purpose appear to be the ketones; *e.g.*, methylethyl ketone, methyl chloride, methyl acetate, and chloroethane. Blends may be selected which avoid fire hazard, such as carbon tetrachloride (50), acetone (50); or perchloroethylene (50), isopropyl acetate (40), and dichloroethyl ether (10). For convenience in commercial practise a simple combination of methylene dichloride and dichloroethyl ether (Chlorex) has been found very effective.

Determination of Oil Content in Paraffins

Diggs and Buchler[6a] have attempted to determine the amount of oil in paraffin wax by a direct refractometer method. To do this it was necessary to isolate wax-free oil and oil-free wax from paraffins. Wax-free oil had a cold test of −22° (−72° F) and an index of refraction of 1.4762 at 60°. Oil-free wax was obtained by filtering wax through an Attapulgus filter clay which selectively adsorbed the oil component from a mixture of paraffin wax and oil. A 54° melting point refined wax, after filtration, had a refractive index $\left(n\frac{60°}{D}\right)$ of 1.4361. If there is much oil several filtrations are needed to give a constant value.

Variations of Index of Refraction with Melting Point

Melting Point (°F)	Melting Point (°C)	$n\frac{60°}{D}$ Refractive Index (after filtration to constant value)
132	56	1.4353–1.4361 (3 samples)
130	54	1.4352–1.4359 (4 samples)
125	52	1.4351 (1 sample)
122	50	1.4342–1.4348 (4 samples)

The method works out well for the routine checking of paraffin of any one refinery, but each refinery must devise its own chart on the basis of synthetic paraffin and oil mixtures. For example at Casper, Wyoming, the paraffin of 122° F melting point gives an index of 1.4342 for 0 per cent oil, 1.4362 for 5 per cent oil, 1.4381 for 10 per cent oil, etc. The method is accurate to 0.1 per cent oil. The authors believe the method to be more accurate and much simpler than the "press method" suggested by Committee D-2 of the American Society of Testing Materials.

Sawyer, Hunter and Nash[26] give the following data for the refractive index of *n*-Paraffin in the liquid state:

Carbon Atoms in Molecule	Melting Point (°C)	Melting Point (°F)	Refractive Index $n\frac{60°}{D}$
21	40.5	104.9	1.4287
22	44.4	111.9	1.4305
23	47.7	117.9	1.4310
24	51.1	124.0	1.4323
25	53.8	128.8	1.4341
26	56.6	133.9	1.4355
27	59.5	139.1	1.4366
28	62.0	143.6	1.4375

Physical Properties of Paraffin Waxes

Density of Commercial Paraffins. The density of a paraffin increases with an increase of the melting point, as shown by the figures given below for the various commercial paraffins:

At	Density of Paraffins with Melting Points of 121° F	126° F	131° F	136° F	141° F
34° F	0.906	0.915 (35°)	0.917	0.922	0.922
45° F	0.903	0.911 (50°)	0.914 (50°)	0.919	0.919
57° F	0.897	0.909 (59°)	0.910 (59°)	0.914	0.915
80° F	0.872 (83°)	0.897	0.902	0.911	0.905 (83°)
100° F	0.849	0.873	0.877	0.896 (95°)	0.903 (95°)
150° F	0.776 (145°)	0.775	0.780 (140°)	0.779 (145°)	0.783 (145°)
165° F	0.769	0.768 (170°)	0.774 (160°)	0.772	0.775
185° F	0.762	—	0.766 (180°)	0.765	0.769

The density curves show an extrapolation from the liquid state values, which plot a straight line, through the temperature range in which the wax is normally solidified, and is taken as representing the density of the wax if it were liquid, or in solution in oil at those temperatures. At 15° (59° F) the observed hypothetical values were found to be in good agreement with those calculated from the equation of Traube

$$d = \frac{M}{\Sigma Av + 25.9}$$

where d is the density at 15°, M the molecular weight, ΣAv the molecular volume (atomic volume of carbon = 9.9, hydrogen = 3.1) and 25.9 is a constant termed "CO-volume."

Molecular Weight of Commercial Paraffins. The molecular weight in relation to the A. S. T. M. melting point is given below. The molecular weights are found by the cryoscopic method, using *p*-dichlorobenzene as solvent.

A.S.T.M. Melting Point (°F)	(°C)	Apparent Oil	Observed Mol. Wt.	Anilin Point (°C)	Calculated Mol. Weight	Corresponding Hydrocarbon C	H
121	49.4	0.5	332	116.7	330	23.55	49.1
126	52.2	0.5	340	117.8	342	24.1	50.2
131	55.0	0.3	355	119.0	359	25.2	52.4
136	57.8	0.3	372	121.0	370	26.4	54.8
141	60.6	0.3	376	122.0	375	26.7	55.4

Mean Refractive Index of Commercial Paraffins. The mean refractive index n of the paraffins in the solid state are as follows:

At	Refractive Index of Paraffins with Melting Points of 121° F	126° F	131° F	136° F	141° F
32° F	1.5337	—	—	—	—
50° F	1.5306	1.5321	1.5348	1.5366	—
68° F	1.5268	1.5278	1.5305	1.5332	1.5350
77° F	1.5169	1.5256	1.5277	1.5311	1.5328
104° F	1.5040	1.5071	1.5103	1.5163	1.5241
122° F	—	—	—	1.5049	1.5087

Influence of Air on Density of Paraffin. Carpenter[4] reported as much as 12 per cent of air in an American refined wax of 132.8° F (56°) melting point. The density of this wax in the air-free condition is given as 0.919 at 60° F (15.6°). Page[22] has shown this figure to be unreasonably high, and has pointed out the probable values for commercial paraffins.

M. P. of Wax (°F)	d_1 Observed at 50° F	d_2 Calculated at 50° F	Volume Per Cent of Air
121	0.900	0.923	2.7
126	0.911	0.927	1.8
131	0.912	0.932	2.2
136	0.913	0.934	1.9
141	0.914	0.935	2.3

The volume per cent of air occluded (not dissolved) is derived from the equation

$$A = 1 - \frac{d_1}{d_2} \times 100$$

Penetration Index of Commercial Paraffin. Penetration readings made with a Universal penetrometer together with readings in hardness made with a Shore durometer are given below for a paraffin wax of 128/130° F (A.M.P.):

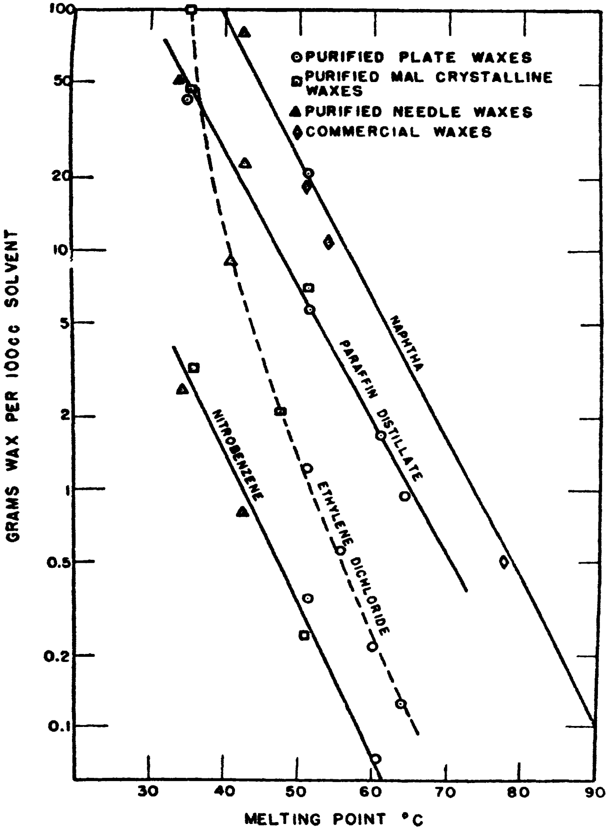
Temperature at—		Penetration (×10) (No. 14, 100 g, 5 sec, 25°C)	Hardness (in units 0–100)
(°F)	(°C)		
40	4.4	2.5	82.0
50	10.0	4.5	79.0
60	15.5	7.5	76.0
70	21.1	12.0	71.0
80	26.7	21.0	62.0
90	32.2	40.0	40.0

The penetration values of the various grades and brands of paraffin wax only differ appreciably from the above tabulated figures in the temperature range of 80 to 90° F. At 90° F the variation can be as great as 50 in the penetration index between the low and high melting refined paraffin waxes.

Solubility of Paraffin in Solvents. Refined paraffin wax of 128/130° melting point has a solubility of 0.0984 gram in 100 ml of 95 per cent ethanol at 25°. It is insoluble in 50 per cent ethanol at 25°. The solubilities of various forms of paraffin at a single temperature in four solvents, of a single paraffin at various temperatures in a number of solvents, have been given by Ferris and Cowles[8a], of the Atlantic Refining Co. (See Figures 16 and 16a.)

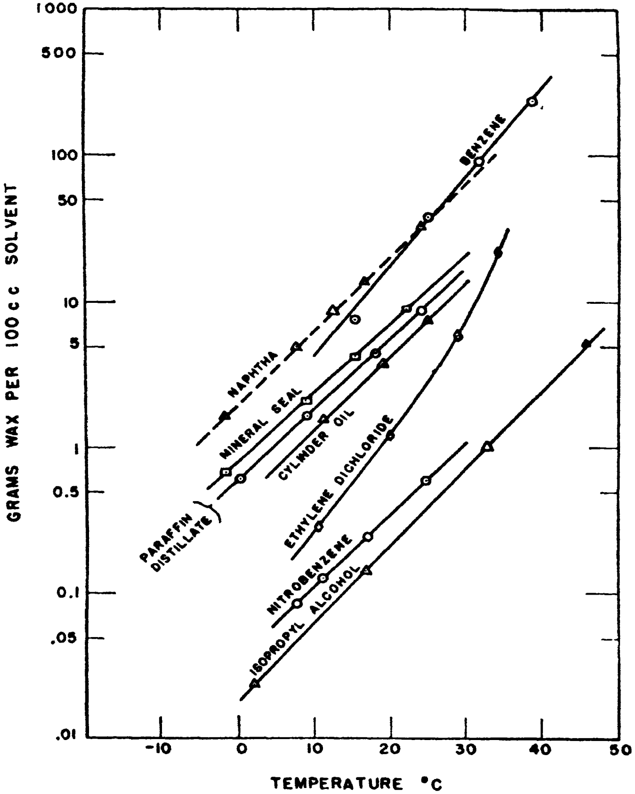
Crystal Habit of Paraffin Waxes

Investigators have studied the crystallization of paraffin wax from petroleum hydrocarbons and from several other solvents. Solid paraffins crystallize either in *plates* or in *needles*, the crystal habit depending upon



From: Ind. Eng. Chem., 37, *1055* (*1945*)

FIGURE 16. Solubility at 68° F of paraffin waxes in non-polar solvents.



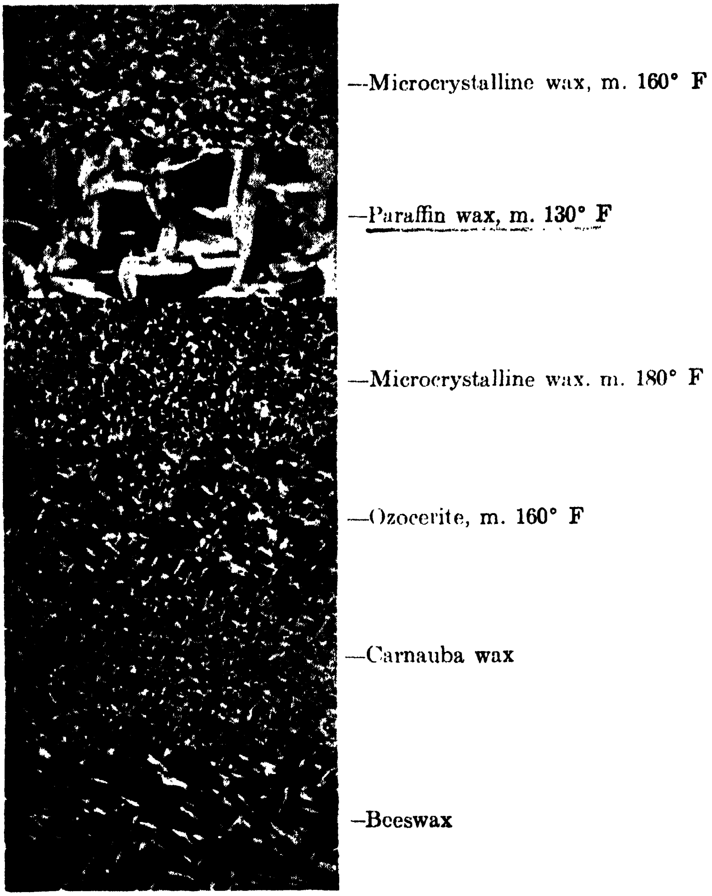
From: Ind. Eng. Chem., 37, *1055* (*1945*)

FIGURE 16a. Solubility of purified plate wax of 125° F melting point in various solvents.

the conditions under which crystallization is effected. Similar crystals are formed when melted paraffin is allowed to cool. Whether the needles and the plates are distinct entities has been a disputed question. Rhodes, Mason and Sutton[25] were inclined to believe that *needles* were *rolled-up plates.* They based their findings on samples of paraffin prepared from slack wax from Pennsylvania crude petroleum. The slack wax had a melting point of 50 to 51° (122 to 124° F), and was separated into several fractions by sweating. The sweating was done by fitting a fine copper screen into a Büchner funnel, closing the outlet, filling it with water above the screen level, and then placing a layer of melted wax on top of the water. When the wax had solidified the water was drained and the funnel and its contents were placed in a large glass cylinder in a thermostat. The temperature was raised very slowly and the oil sweated from the wax was collected in fractions. The average molecular weight of the material in each fraction was determined by the cryoscopic method, using naphthalene as solvent. In this way they secured fractions with melting points of 110.0°, 117.0°, 121.8°, 125.0°, 129.2°, and 134.0° F. The average molecular weights were 415, 403, 417, 432, 443, and 445 respectively.

The behavior of each fraction was then studied microscopically. The specimens were heated and their ratios of cooling regulated by means of an insulated hot stage. The hot stage of an ordinary chemical microscope was electrically controlled to within 1° and used with a microscope equipped with Nicol prisms for observation with polarized light. Photomicrographs were made of the crystals during the process of development. In every case the waxes started to solidify in small plates. On rapid cooling these plates assumed a polygonal outline, or outlines. As changes were followed under the microscope it was seen that the edges of the plates actually rolled up, and that from these rolled edges there developed needles tangent to the original plate. The needles then elongated and became better defined. Finally the mass solidified completely to a coarse-grained structure of plates and needles. On rapid cooling the wax consisted chiefly of fine needles with a few coarse plates. Crystallization from kerosene, acetone or xylene may be more easily controlled. On very slow cooling plates develop for the most part with only few needles.

The crystals referred to above are *macrocrystals,* in contrast to the *microcrystals* found in the so-called "amorphous" or "microcrystalline" paraffin. The wax precipitated from residual oils is of the amorphous variety; that from the distillate may be either amorphous or crystalline. If a distillate contains crystalline wax only, it will generally press satisfactorily, and the slack wax will offer no difficulty during sweating. According to one scientific theory both forms are considered crystalline; the difference is a matter of crystal size, and the microcrystalline structures are presumably caused by the viscosity of the associated oils and by asphaltic matter. The other theory is that the greater part of the "amorphous" wax is truly amorphous—a characteristic of wax having hydrocarbons with side chains, but that such wax when distilled will yield normal crystalline hydrocarbons on cracking. Padgett, Hefley, and Henriksen[21] arrived at



Courtesy Bareco Oil Co.

FIGURE 17. Crystal habit of waxes. Magnification 150x.

the following conclusions about crystalline structure by microscopic methods using hanging-drop and depression slides of melted material and material precipitated from acetone solution. The crystals from residual oils, petrolatum, and heavy raw-wax distillates, were small even after substantial removal of the bitumen and repeated precipitations from acetone, and were much smaller than the smallest crystals found in slack wax.

Petrolatum wax tended to form microplate-like crystals. In the initial stage of crystallization of slack wax a few plate-like and massive crystals were observed. In the crystallization of refined wax a large number of plates were formed, from which needle crystals developed. *Leaflets* are probably a transition stage in the transformation of plates to needles. *Mal crystal* forms are regarded as an orientation of plate and needle forms.

Microscopy of Waxes. Wax crystals are formed, according to Taub and Zweig,[27] by dissolving the wax in the proper solvent at the solution temperature of the wax in question and allowing to cool spontaneously to room temperature. Although the waxes represent mixtures of several constituents, each wax will tend to give one or at most two types of crystal formation. Because of the dual nature of amylamine as solvent and chemical reagent, it was found very suitable for wax crystallography. Butyl alcohol was also used as solvent. Some typical crystal formations obtained with beeswax, carnauba wax, candelilla wax, and ozocerite, using amylamine, have been described, and also some odd types of crystal formations from potassium stearate in butyl alcohol and from cerotic acid in amylamine. In mixtures of waxes some idea of the main constituents present may be gained from the appearance of the crystals. (Figure 17.)

Waxes of high tensile strength are a closer cut and have a limited range of melting points in the intermediate melting point series; they, therefore, do not contain the long needle crystals. The high tensile strength is brought about by the plate crystals which tend to slide over each other, making it possible to pull paraffin out like taffy. When the paraffin is chilled, however, it may become quite brittle, and this same tendency is noted in wax mixtures of which paraffin is one of the principal constituents.

Grades of Paraffin Wax

American Paraffin Wax. Following is a list of the most important grades of American paraffin wax:

Paraffin Wax	Melting Point, °F
Fully refined	118–120
	123–125
	128–130
	130–132
	133–135
	138–140
	143–145
Special refined	124–126
	128–130
White scale	124–126
Yellow scale	124–126
	125–127
	128–130
	135–137
	138–140

Paraffins of a specified melting point are obtainable in greatly varying tensile strengths, showing *short* or *long* characteristics as desired.

The relation between the melting point, refractive index, flow point, and hardness of each of the several grades of American paraffin wax is shown below:

M. P. (°C)	$n_D^{80°}$	Flow Point (°C)	Durometer Hardness	
			30° C	4°C
42.4	1.4219	37.0	19.5	48
50.0	1.4253	40.5	33.0	90
55.6	1.4278	45.0	34.5	91
61.0	1.4316	48.5	34.0	89
64.0	——	55.5	34.0	88
70.0	1.4357	63.0	31.0	86
75.0	1.4484	59.0	30.5	86

Asiatic Paraffin Wax. The Asiatic paraffin waxes are refined from the crudes of the Netherland East Indies, which are of exceptionally good quality. The commercial grades of the Asiatic Petroleum Corporation are as follows:

	Melting Point, °F
Fully Refined Paraffin Wax	128–130 (A.M.P.)
	138–140
	143–145
	148–150
	158–160
	163–165
Paraffin Wax Ceresin	190–195 (A.S.T.M.)

The relation between the melting point, softening point, and hardness (at two different temperatures) is given below.

Grade °F Range	Actual M. P. (°F)	Softening Point (°F)	Durometer Hardness	
			34° F	88° F
138–140	138.0	118.0	82	74
143–145	144.5	124.0	83	75
148–150	147.5	130.0	85	78
158–160	160.0	132.0	92	80
163–165	163.0	132.5	93	82
190–195	196.0	170.0	100	97

The fully refined waxes are white in color, and the paraffin wax ceresin is yellow in color.

Aristowax. Paraffins of similar properties to the Asiatic are refined by the Union Oil Co. of California and bear the trade name "Aristowaxes." *E.g.*, Aristowax m. 145/150° F (A.M.P.) and 160/165° F (A.M.P.). The former has a penetration value of about 14 at 77° F, the latter a lower penetration.

Uses of Paraffin Wax

It has been estimated that about 600,000,000 pounds of paraffin waxes are used each year for industrial purposes. The uses of crystalline paraffin wax are shown below:

Baking powder containers
Barrel linings (wooden)
Bottle cap liners
Bread wrappers
Builders' papers
Butchers' papers
Butter casks
Cable junction
Candles
Candy wrappers
Chewing gum wrappers
Condensers (paper-metal foil)
Cork inserts
Citrus fruits (coating)
Crayons (artists and pastels)
Crayons (ordinary)
Delicatessan trays
Dictaphone records
Dormant plant wax
Drinking cups
Explosives
Fabric sizing
Fireworks
Fish paper
Floats
Floor polishes
Florists' paper
Flood containers
Fruit wrappers
Glassine
Instrument transformers (electrical)
Kitchen rolls (waxed paper)
Label paper
Laundry tablets (bluing)
Leather (currier wax)
Match wax
Milk bottles (paper)
Milk caps
Paint
Phonograph records
Printing ink
Removing feathers from fowl
Rubber manufacture
Sash cord
Shoe creams
Silver polishing blocks
Soda straws
Terminal bases (electrical)
Tapers
Waterproofing textiles
Wire coating

The oldest use of paraffin wax is in the making of candles, the paraffin wax being blended in large amounts with stearic acid. This use of paraffin is still one of the largest. An enormous amount of paraffin wax is used for waxing wrapping paper and paper containers for packaging food. A large amount of the softer paraffins is used in the manufacture of matchsticks, and in the waxing of fruits and vegetables. The softer quality is used for miner's lamps, and household-, ship-, and hand-lamps. The peculiar properties of paraffin make it a useful material for many purposes, and as it is getting more plentiful and less expensive, its applications are extending. According to Thorpe, paraffin is used for waterproofing cloth, leather, walls, cartridges, and wrapping paper; for coating the inside of vessels to prevent rust and decay; for electrical insulation; for splints in surgery; as a medium for salves; for extracting perfume from flowers; for waxing thread, floors; for heating-baths in laboratories; and for numerous other purposes. Wooden barrels, kegs, and shingles are often waxed.

Mixtures of crude or purified paraffin wax and crude petrolatum were used successfully for lubricating blocks and ways in the launching of European ships. The material is thinly spread on the ways in two applications to the wood; the top layer is finished in green soap and linseed oil, then covered thinly with mineral oil.

Paraffin wax-lined oak barrels have proved to be excellent containers for dry skim milk, especially for export shipment. The barrels are moisture- and possibly gas-tight and may be floated ashore and stored in exposed places without damage to their contents. They cost about 1 cent per pound of powder more than the slack barrel.

Softer Paraffins

Slack Wax. Mixtures of crude petroleum wax and oil, usually formed by separation from waxy oil, comprise *slack wax.* The consistency of slack wax may be soft or semi-solid and the oil content is normally from 10 to 50 per cent. The term is usually applied to distillate products, and is given to a mixture of oil and paraffins of many widely different melting points. A product of 19 per cent oil is extensively used in luster cleaners.

Sweat Wax. The term "sweat wax" is sometimes confused with "slack wax" from which it differs in that the *sweat wax* is a mixture of oil and paraffins of a rather limited range of melting points in the lower melting point series.

In the sweating of slack wax the oil which is drawn off contains a large quantity of wax crystals. This mixture when chilled at only a moderately low temperature will yield on sweating the paraffins of the higher melting points and a sweat oil containing crystals that melt at 60° F and also some that melt at somewhat higher and lower temperatures. Sweat wax therefore is a solid mass at 60° F or thereabouts but appears to have 60 per cent or more of oil at 80° or 90° F.

Sweat wax is used whenever it is essential to secure wax penetration, as in the textile and paper industries. It is used in wax emulsion with naphtha, or without it. A mixture of 87 parts of sweat wax, 11 parts of bentonite, whiting, or other mineral filler, and 2 parts of pigment, makes a paint suitable for closing the mesh of woven fabric, imparting color and rainproofing.

Tent cloth can be treated with sweat wax using naphtha as a carrier. In water emulsions it is of value in waterproofing krafts. Bags for holding chemicals can be prevented from rotting by weaving the material with some form of scale wax or sweat wax-treated thread.

Uses of the Softer Paraffins. The softer paraffin waxes are available in crude as well as refined forms and at various melting points. They contain an amount of oil sufficient for penetrating the material which is to be paraffined. In the fabrication of cotton duck and canvas the thread is treated with a crude scale wax of 124° F melting point, to impart waterproofing. A scale wax of 136° F melting point is used with materials where a drier, non-greasy, finished product, which is not very susceptible to atmospheric change, is desired.

Smaller quantities of carnauba, gilsonite, or high melting point asphaltum are necessary in the formulation of waterproofing compound when a relatively high melting point scale wax is used; at the same time a thinner application will give the article the required degree of waterproofing. The high melting scale waxes are hence sometimes referred to as "textile proofers."

A *scale wax* with A. S. T. M. 145–150° F melting point is used in the kraft paper industry, for builder's papers, cement bag stock, roofer's felts, car liners, and heavy kraft wrappings. Scale wax is more pliable than block paraffin and will not crack. An example of this type of paraffin is found in a wax known under the trade name of "Amprol No. 2," a product of the Atlantic Refining Co.; this wax has a Saybolt Universal viscosity of 60 to 70 at 210° F. The color of the wax is a light walnut which is not suitable for white krafts, but good for unbleached krafts; the wax can be applied at working temperature of 260 to 280° F to secure maximum saturation.

Amprol No. 3 is the trade name given to a blended wax which consists of crystalline wax and a highly penetrating oil. It is solid at room temperature but liquid at 100° F. Amprol No. 3 is used for waterproofing spool winders in textile mills. It will moistureproof close-grained products such as papier-maché. It penetrates very well at 160 to 180° F, carrying wax with the oil. It aids in the extrusion of rubber. Amprol No. 3 is also used with hard rubber, paper tubing, and hard fibrous products.

Scale waxes of 124 to 126° F melting point are used for matches and crayons. For this purpose they must contain less than 1 per cent of combined oil and moisture. Petrolatums of high melting point (140° F) are used in much the same way as the scale waxes for the waterproofing of kraft papers, cotton ducks and canvas. For this type of petrolatum the Saybolt Universal viscosity at 210° F is about 40 seconds; the finish is less dry than that of the scale wax.

In the formulation of flexible artificial ceresin the scale waxes may be used to advantage with or without paraffin. The use of a scale wax with too much oil or of slack wax may yield a product with large macrocrystals of paraffin tending to destroy the flexing or elongation. If a low melting scale wax is used it is preferable to limit it to 2 or 3 per cent when used in conjunction with refined paraffin wax.

Paraffin residue is a low-grade product. One of the trade names for this is "Oxprol" (Atlantic Refining Co.) which is used in foundries for making up core sands, replacing linseed or core oil.

	Oxprol	Linseed Oil	Core Oil
Iodine Number	230	185	159
Pour Point	0°	+5°	0°
Flash Point	225°	535°	175°
A.P.I. Gravity	16.6	19.5	19.3
S. U. Viscosity at 100	295	173	178
Color A.S.T.M.	8+	3¾	4

A core recipe for a steel casting plant is given below:

2,000 pounds	Cedarville Green Sand (4–5% water content)
53½ pounds	Truscon Cereal Binder
8 quarts	Oxprol

Mix ingredients. Mold the sand. Use the rods when cores are large. Spray cores with core wash, and bake in oven at 420–450 F. Remove cores from oven, cool and use.

MICROCRYSTALLINE WAXES—PETROLATUM AND PETROLEUM CERESIN

Crystalline Types of Waxes

It was observed many years ago in the sweating of the solid paraffins at the petroleum refinery that three crystalline manifestations of hydrocarbons are involved. These are known as "plate," "mal crystal" and "needle." It was also recognized that the relative proportion of these types of crystals not only bears a relation to the source of the crude, but to the method of handling the wax in the sweating and filter-press operations.

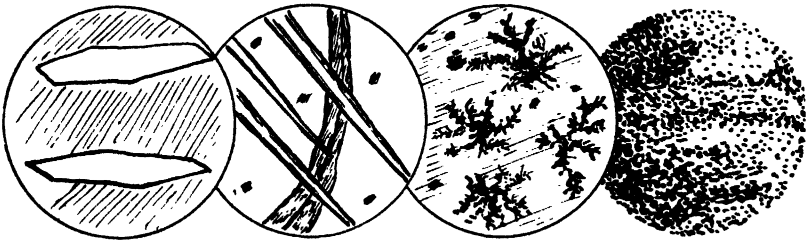


Plate *Needle* *Malcrystalline* *Microcrystalline*

FIGURE 18. Types of wax crystals obtained from dilute solutions of the wax in non-petroleum solvents.

Present refining methods, particularly sweating, have a tendency to remove the ill-defined or "mal crystals" and the "large needles" which are common to the lower hydrocarbons, so that the finished waxes for the most part approach the plate type in which the crystals are hexagonal plates. The microcrystalline waxes now recovered from the *still residuum* are of the plate type, but the crystals are of extremely small or microscopic size.

It is possible for the plate type of crystal to undergo a transition to the needle type, particularly if the wax has not been sufficiently sweated to remove most of the lower hydrocarbons. In some instances the needles have been regarded as rolled-up plates.

A crystalline structure of distinctly larger size than what is generally regarded as "microcrystalline" is referred to as "macrocrystalline." The word "amorphous" still persists in the trade to describe microcrystalline structure. The term "amorphoid" might be more descriptive, since it would indicate that the structure, while not actually amorphous, approaches the amorphous condition.

Microcrystalline Waxes

A microcrystalline wax derived from petroleum has been defined as a "solid hydrocarbon mixture, of molecular weight averaging higher than paraffin wax, possessing plastic properties, separated entirely from part of crude petroleum commonly designated as heavy lubricating and cylinder oil stocks, and having a minimum kinematic viscosity of 5.75 centistokes at 210° F and a maximum penetration of 60 at 77° F, determined by A.S. T.M. method D5–25."

In the preparation of the microcrystalline waxes, when dewaxing is conducted on petroleum stock or "slop wax," it is far better accomplished by modern procedures involving the use of centrifugal force than by other means. The centrifugal process for the production of bright lubricating stock is in nearly universal use in the United States. Considerable quantities of "long residuum" are also dewaxed centrifugally, as are also the heavier lubricating distillates.

Jones and Blachly[13] relate that there are several conditions which must be fulfilled in the preparation of amorphous (microcrystalline) wax in order that it may be satisfactorily removed centrifugally from the liquid phase containing the lubricating stock. There must be sufficiently complete precipitation of the wax and the precipitate must be coarse enough for its rapid and complete removal. These factors are controlled by the nature of the solvent used for diluting the lubricating stock, the amount of solvent used, and the rate, extent, and character of the chilling. The microcrystalline waxes offered in the market are often designated by their method of preparation and physical properties. For example, the name *petrolatum wax* applies to a microcrystalline wax refined from petrolatum stock. Usually a sticky wax of about 155° to 170° F melting point, and a penetrometer value of more than 25 is implied. The waxes that are much harder, more oil-free, of higher melting point (180° to 195° F), and which have a penetrometer value of less than 25, are known as *petroleum ceresins*.

Petrolatum Group

Petroleum Jelly. Petroleum jelly has been defined as petrolatum, soft and salve-like, consisting of certain petroleum solids in admixture with oil. For pharmaceutical purposes the U. S. Pharmacopœia has defined petrolatum as a "mixture of hydrocarbons, chiefly of the methane series, obtained by distilling off the lighter and more volatile portions from petroleum, and purifying the residue." The British Pharmacopœia defines petrolatum as "a semi-solid mixture containing soft members of the paraffin series of hydrocarbons; usually obtained by purifying the less volatile portions of petroleum."

Petroleum jelly is prepared from the residue left in the stills after a distillation of petroleum *in vacuo*, or from the residue or sediment deposited in tanks containing crude petroleum, of which large quantities have collected in the storage tanks in the oil districts of Western Pennsylvania. The substances known commercially as *Cosmoline* and *Vaseline* are now made on a large scale from residues, but more largely from what are termed "reduced oils"; that is, crude oils from which the lighter fractions have been removed by distillation. These lighter fractions include the paraffin distillate. Reducing is carried out under diminished pressure, by what is known as the "vacuum process," in which the heat is not applied directly to the still bottoms, but by means of coils of pipe, through which superheated steam is passed. These reduced oils can be brought to 338° (640° F fire-test without acquiring any pyrogenous odor. They are then filtered through bone black, in chambers kept at 43.3° to 54.4° (110° to 130° F), or in some cases higher, to give the greenish-red fluorescent "cylinder stocks" valued as lubricants. The crude oil tank residues are purified in a similar manner.

The United States Dispensatory gives methods of testing the source of petrolatum and its evaluation. In warm ether, American petrolatum dissolves freely into a clear solution exhibiting strong blue fluorescence, and the liquid remains clear, or at most becomes slightly turbid, on cooling. German petrolatum, on the contrary, is said to form a thick solution with warm ether, and to give a considerable deposit on cooling. Russian petrolatum is described as dissolving completely in warm ether, giving a clear solution which becomes turbid on cooling.

Petrolatum, as made from American petroleum and first discovered by Chesebrough, contains hydrocarbons of the paraffin series, such as *hexadecane*, *heptadecane*, *octadecane*, etc., probably up to *dotriacontane*, together with hydrocarbons of the olefin series, *cetene*, *heptadecene*, *octadecene*, etc. These olefin hydrocarbons are less concrete than the corresponding paraffins, and give petrolatum its oleaginous characteristics.

Petrolatum has a specific gravity of 0.820 to 0.850 at 60°. It is insoluble in water; scarcely soluble in cold or hot ethanol, but soluble in boiling absolute ethanol, and readily soluble in ether, chloroform, turpentine, petroleum benzin, benzene, and fixed or volatile oils. The melting point ranges from 45° to 48° if of U.S.P. quality.

Liquid petrolatum is made by distilling the residuary liquid between 330° and 390° obtained after removing the lighter hydrocarbons from petroleum. It is purified and decolorized by first treating it with sulfuric acid and then with sodium hydroxide and passing it while hot, through animal charcoal. On cooling, some solid paraffins will separate; the liquid is then redistilled, and the portion below 360° rejected. Liquid petrolatum is a colorless, odorless liquid, having a specific gravity varying between 0.870 and 0.940 at 25°, according to the grade.

Petrolatum Wax. Petrolatum wax or "crude petrolatum wax," as it is also called, contains more than 10 per cent of oil; it is obtained from the acid-treated petrolatum stock, containing a fairly high percentage of wax, by treatment with naphtha and centrifugation of the solution to remove excess oil. This wax may again be put into solution and recentrifuged to remove excess oil. A method of preparing the crude wax is that of Diggs, Beard and Page,[6] in which the "bottoms" or residues of the still are treated with sulfuric acid to remove asphaltic material; the oil is neutralized, filtered, and chilled to a temperature near freezing, whereupon the petrolatum wax precipitates. The latter is dissolved in ethylene dichloride or in naphtha, and cooled to a temperature at which the high-melting crystalline fraction precipitates, usually at 100 to 70° F. This paraffin is removed (worked up separately) and the resulting solution comprising the microcrystalline wax is cooled below 40° F to precipitate out the adhesive wax fraction (petrolatum wax), which is separated and ready for use. The petrolatum wax may however be redissolved in a selective solvent and reprecipitated in a paler colored product of a somewhat sharper and higher melting point. In the method described the naphtha is 54° A.P.I. gravity and the recoveries of wax are made from a 20 per cent naphtha solution. The second centrifuging removes a wax that melts at about 147° F and possesses high adhesiveness. This adhesive wax may contain as much as 21 per cent of oil, but the oil content may be reduced by reprecipitating the fraction from naphtha, by pressing, or any suitable means. If the oil content is reduced to about 18 per cent, the melting point is raised to 151° F. Acetone and benzene may be used instead of naphtha. The crude petrolatum wax may be fractionated into waxes having melting points about 165° F, between the temperature ranges of 150 and 160° F., 140 and 150° F. The grade of soft adhesive wax of the Gulf Refining Company, known as "Petrowax" is of this description.

Salt Creek crude oil is reduced, by the Standard Oil Company (Indiana), to 40 per cent of "bottoms," diluted with naphtha, and centrifuged to yield a yellow microcrystalline petrolatum, melting at 150–175° F. The petrolatum is also prepared by filtering the crude oil through clay, which is then exhausted with Chlorex or furfural.

Petroleum Ceresin Group

Petroleum Ceresin Waxes. Low penetration waxes are prepared by dewaxing heavy wax-bearing distillate consisting essentially of hydrocarbons of cylinder-stock viscosity and tarry constituents removable by solvent extraction of the oil. The treated stock to begin with has a pour point of 60 to 80° F. This crude petrolatum comprises a low pour point oil, "Vaseline" bodies, and waxes having a melting point as high as 190/195° F, made up of 35 to 50 carbon atoms in the chain. Formerly this black crude petrolatum was sold for ordinary technical use, but it is now being turned into usable oil and valuable waxes; the Vaseline-like residuum being of little or no use. In extraction with solvent, a saturated solution of the petrolatum wax is obtained at a temperature of about 200° F, and when the temperature is dropped to 100° to 120° F the wax is precipitated and removed by filtration. The waxy constituents separating may constitute one-third or perhaps one-half of the petrolatum. The product extracted must then be mixed with a coarse decolorizing clay on the filter and filtered hot. The first filtrate is pale in color; the last is quite dark. An alkaline clay, such as Attapulgus clay, is used for this filtration, and the clay is reburnt for further use. Pure white petroleum ceresin commands a higher price in the market than the yellow, and is substantially free from occluded oil.

The petroleum ceresin waxes vary in color from dark brown to white. Their molecular weights range from an average of 450 to 1000 and their setting points are above 71° (160° F). Generally the crystals of ceresin waxes are much smaller than the small crystals of refined paraffin waxes.[2]

A microcrystalline wax of very high melting point, namely 195/197° F, has been offered on the market. This wax has a softening point of 192/195°; a penetration 100 grams at 77° F (A.S.T.M. D5–25) of 5; an oil content of almost *nil*. It has great strength and toughness and is flexible in a thin film at low temperatures. It is refined at Kilgore, Texas.

Brands of Microcrystalline Waxes

There are many brands of microcrystalline waxes, and these brands differ because of the character of the raw petrolatum stock, and the method of refinement. There are also gradings according to color; black, brown, dark amber, amber, pale amber, pale yellow, and white waxes. These gradings are associated with the melting points, for example "black amorphous 180/185," or "pale yellow 180/185." Patentees have associated brand names with their patent specifications. Rau[24] states that in his candle composition, consisting of "beeswax, amorphous petroleum wax, and a wax-hardening agent," one can use "Petrowax" of the Gulf Refining Co., or "Superla Wax" of the Standard Oil Co. of Indiana.

Selective Solvents for Extraction of Wax

The solvents which are used for extracting the waxy constituents vary with the refinery methods and the character of the treated stock. Oil refineries in general are not prone to disclose what they use, except through their patents. Specific solvents are dichloroethane, dichloropropane, dichloroethylene, trichloroethylene, and other halogenated organic compounds. Such solvents are also sometimes diluted with benzene or naphtha as the case may economically require. Other selective solvents are nitrobenzene, aniline benzophenone, dichloroethyl ether.

Polar diluents, such as methylethyl ketone, are generally used with nonpolar solvents in the dewaxing of heavy wax-bearing oil consisting essentially of cylinder-stock viscosity. The purpose of the polar solvent is (1) to aid in the formation of more definite microcrystals, (2) to increase the rapidity of filtration, (3) to make it possible to precipitate the wax at a higher chill temperature, and (4) to reduce the amount of total diluent needed to effect the proper separations. The oil is mixed with about 3 to 4 parts of combined polar and nonpolar solvent, or a proportion of the latter sufficient to prevent separation of the oil from the mixture at a predetermined chill temperature, say $-10°$ F. The mixture is then chilled and the precipitated wax removed.

Govers[10] found that the rate of filtration can be substantially increased by the use of ethylene dichloride as the nonpolar solvent, followed by chilling to precipitate the wax constituents (of higher melting points), and filtering in the presence of a polar substance of the character of SO_2, acetone and methylethyl ketone to cause further precipitation of wax, the polar substance comprising about 5 to 10 per cent by volume of the mixture of wax-bearing oil and nonpolar diluent. The solvent is recovered after the filtrate has been dewaxed.

Jones[14] selectively extracts the oil from a petroleum stock such as a distillate from a Mid-Continent oil by dissolving the oil content of the stock in a mixture comprising 1,1,2- or 1,1,1-trichloroethane and another material such as trichloroethylene, dichloroethylene, benzene or naphtha, or ethylene dichloride and a propylene dichloride; the wax being removed from solution at a temperature sufficiently low to effect its precipitation.

Knowles[15] has proposed to mix the wax-bearing mineral oil with aliphatic ketones, *e.g.* dipropyl ketone and methylethyl ketone in such proportions that at −18° the solvent action on the oil is complete, but there is substantially no solvent action on the solid waxy constituents. The mixture is chilled to effect wax separation. Knowles also advised the use of dialkyl ether, such as acetal, as a selective solvent for the same purpose. Gross and Overbaugh[11] suggested treating the wax-bearing oil with 4 parts of commercial methylisobutyl ketone, and chilling the mixture to about −10° F to precipitate the wax and remove it.

Manley[17] proposed the use of furfural at a temperature of 95° at which the wax-bearing is in an entirely liquid phase. The naphthenic constituents are then separated from the hot mixture and removed; the remaining mixture of relatively paraffinic, wax-bearing oil and furfural is combined with additional furfural and benzene and chilled to bring about wax separation.

Propane Extraction of Microcrystalline Wax from Petrolatum. Petrolatum produced in normal refining operations by the cold settling or centrifuging of residual steam refined stock, or cylinder-stock distillate, is known to contain from 25 to 75 per cent of high melting point wax and 75 to 25 per cent of "bright stock." Tears[28] proposed a method of de-oiling petrolatum wax using propane. The petrolatum wax of Pennsylvania crudes is treated in this manner. In the Tears process the propane is kept in a cold storage tank from which it can be drawn into an auxiliary tank, so that it can be fed with a suitable amount of petrolatum into a heater, thence to a cooler and over to a series of large drums known as "chillers" and "settlers," which are also linked up with a plentiful supply of propane. With chillers and settlers full to capacity, the liquid contained in each of three tanks to the top of the try cock may be 1800 gallons, of which 1325 gallons would constitute propane and 475, petrolatum to be stripped. The temperature is reduced to −45 °F, which corresponds to atmospheric pressure. The agitation of the mixture by entry of warm and cold propane and the boiling by evaporation makes a perfectly uniform mixture from which the solid wax may be settled in an hour or two. The bright stock has good color, and a pour test of 0 to 5° F.

To remove the last traces of oil from the wax, or propane from the oil, additional adjuncts known as "wax and oil strippers," comprising a "wax stabilizer" and an "oil stabilizer" suitably equipped with steam coils, are employed. In this manner a wax of high melting point can be produced. (see p. 247).

Precipitated residue from propane extractions are sometimes referred to as "petroleum polymer." The polymer material is black in color, has a high melting point, around 139° (282° F), and a softening point as low as 27° (80° F). It is soft at 27°, but firm at lower temperatures. This inexpensive material is of considerable value in laminating foil to kraft paper and large quantities are used for this purpose. It is applied at a temperature of 205° (400° F).

Manley Process of Dewaxing Wax Bearing Oils. In the Manley[18] process the wax-bearing oil is mixed with about twice its volume of a diluent comprising propane and butane, and the dilute mixture is chilled while flowing in a confined stream in indirect heat-exchange relation with a cold portion of the diluent undergoing refrigerative evaporation. The dilute stream is chilled to a temperature of $-18°$ or below to solidify the wax. The solidified wax is separated from the cold mixture, and the diluent contained in the dewaxed mixture is subjected to refrigerative evaporation in indirect heat-exchange relation with the aforesaid confined stream of dilute mixture to effect its cooling. The patent describes the apparatus required and its arrangement. According to Manley, the cold dilute mixture while under super-atmospheric pressure is subjected to filter-pressing, forming a filter cake of solid wax. A stream of dewaxed filtrate is continuously removed from the filter and sufficient pressure is imposed on the filtrate stream to prevent substantial vaporization of the diluent from the oil during filtration. Microcrystalline waxes of both softer and harder penetration are thus recovered.

Characteristics of Microcrystalline Waxes

Microcrystalline waxes have a high melting point and are all of about the same molecular weight. The hydrocarbons of which they are composed are said to have chains twice the length of those of the macrocrystalline waxes. It is believed that the chain is doubled over and somewhat intertwined with itself, which would make its effective length in some respect no longer than the regular paraffin chain. These amorphoid waxes, even in the higher melting points, may be quite soft and adhesive; but they may also be quite hard and firm like beeswax. In general most of the microcrystalline waxes have a high degree of plasticity which makes them valuable for uses where plasticity and high melting point are desirable.

There are several theories with respect to the cause of the microcrystalline structure. One theory is that this structure is owing to a so-called natural inhibitor, possibly a long chain carbon, as may be found in asphalt. If such an inhibitor could actually be isolated it would when blended with crystalline wax actually yield an amorphoid wax. Another theory is that microcrystalline waxes are associated with heavy residual stocks and cannot be separated completely from the high pour oil and therefore can form no well-defined crystals; paraffin waxes, however, are associated with only light distillates and can readily be separated as macrocrystalline types.

There is some speculation as to whether an unsaturated hydrocarbon such as $C_{34}H_{66}$ might be a factor in causing the so-called oiliness of these waxes. *Tetratriacontadiene* (prepared by electrolysis of sodium oleate solution) and other higher homologs of the unsaturated series have been studied by Dover and Helmers[8] for the lubricating value which they give to oils. The $C_{34}H_{66}$ hydrocarbon has a melting point as low as 20.5 to 21°; a density (22°) of 0.8410; an iodine number of 102.5; refractive index (sodium light, 20°) of 1.4655; and dielectric constant (25°, 130 kilocycles) of 2.82. By hydrogenating the yellow paraffin using platinum oxide as a catalyst and ferrous sulfate as a promoter, a white solid paraffin, m. 71.5 to 72°, which corresponds to the normal saturated paraffin, *tetratriacontane*, is formed.

When a petrolatum wax is added to melted paraffin it acts like a solute with paraffin the solvent, the melting point of the blend is greatly elevated, and the crystallization of the paraffin is depressed. The behavior is that of a two-phase system until about 15 per cent of petrolatum has been added. After that the paraffin begins to lose its identity, and this is at first manifested by furrows on the surface of the congealed melt. When the petrolatum wax is 30 per cent of the whole the furrows begin to disappear entirely. With the addition of 15 per cent of the petrolatum wax the melting point of the paraffin is elevated from 130 to 160° F (see table below). Were there only a single phase system the actual rise would be from 130 to 160° F, based upon a straight line curve plotted with melting point against the percentage of one of the components.

% Petrolatum Wax 180/190	% Paraffin Wax 128/130	M. Pt. (A.S.T.M.) (°F)
0	100	130
1	99	131
2	98	133
3	97	136.5
5	95	144
10	90	153
15	85	160
20	80	163.5
30	70	168
40	60	173.5
50	50	177
65	35	180
80	20	182.5
90	10	184
100	0	188

Physical Constants of Petroleum Waxes

The physical constants for petroleum waxes were determined in a comparative way by Buchler and Graves.[3] The waxes were *paraffin wax*, *petrolatum wax*, *slop wax*, and *rod wax*.

Paraffin wax is listed as having 14 hydrocarbons ranging from $C_{18}H_{38}$ to $C_{32}H_{66}$, solidifying between 27.0 and 68.9° (80.5° and 156.0° F). Petrolatum wax has 9 hydrocarbons ranging from $C_{34}H_{70}$ to $C_{43}H_{88}$ inclusive. Its solidifying range is 71.0 to 83.8° (159.7 to 182.7° F); refractive index $n\frac{84°}{D}$, 1.4323 to 1.4378; density at 84°, 0.7706 to 0.7803; molecular weight 474 to 603.

Slop wax has 13 hydrocarbons ranging from C_{26} to C_{43}; solidifying between 55.7 and 83.3° (132.2 and 182.0° F). Rod wax has 8 hydrocarbons ranging from C_{35} to C_{41}; solidifying at 73.9 to 82.5° (165.0 to 180.5° F).

The petroleum waxes were all taken from a Salt Creek, Wyoming crude. The paraffin wax was obtained by pressing the wax distillate at −17.8° (0° F); the slop wax from the heavy distillate in the coking process; the petrolatum was centrifuged from residual stocks at −17.8° (0° F); and the rod wax collected from the sucker rods in the field.

Each wax was recrystallized from ethylene dichloride at 4.4° (0° F) until a wax of constant melting point and index of refraction was formed. Such fractions were then used as a basis for determining the composition, and for establishing the fact that the series is a homologous one of saturated hydrocarbons irrespective of whether the wax is crystalline or approaches the amorphous state.

The petroleum ceresins have a specific heat value of 0.6. The latent heat of fusion is 35 to 39 calories per gram. The dielectric constant (S.I.C.) is about 2.4 at 30°, and declines to 2.1 at 85°. The dielectric strength (K.V.) is 50 plus at 30°, 31 to 38 at 70°, and 35 to 41 at 100°. The optimum vapor pressure at 120° is 0.001 (mm Hg).

Specific Gravity of the Microcrystalline Waxes. The specific gravity of microcrystalline hydrocarbon wax is quite different in the molten state from that of the solid state, as is also true of other waxes. Measurements were made by Bulatkin[29] of the petroleum ceresin, Petrosene A, m. 163.8° F (73.2°), the gravity being based upon water at 15°. The results are here tabulated:

	°F	°C	Specific Gravity
In Solid State	44	6.67	0.9343
	60	15.56	0.9294
	80½	26.90	0.9236
	127	52.78	0.8921
	160	71.11	0.8300*
In Liquid State	170	76.67	0.8025
	180	82.22	0.7999
	200	93.33	0.7935
	212	100.00	0.7890
	240	115.56	0.7805
	280	137.78	0.7610
	320	160.00	0.7535
	360	182.22	0.7410
	400	204.44	0.7380
	438	225.56	0.7140

*Computed value.

The specific gravity of the molten wax increases fairly rapidly as the wax cools down to the approaching resolidification point. During the critical stage of solidification or until the soft wax reaches a temperature low enough to becomes a uniform solid, there is a pronounced increase in gravity. On lowering the temperature further, there is a less marked drop in the gravity of the wax in the perfectly solid state.

Coefficient of Expansion of Microcrystalline Waxes. The coefficient of expansion of a wax can be determined from the change in specific gravity with change in temperature, *e.g.* by the formula $d^1 : d = 1 : 1 - Dt$, where d = density of body at initial temperature, d^1 = density of body at observation temperature, D = cubical coefficient of expansion, 1 = volume of body at initial temperature, and t = difference between the initial and the observation temperatures. From the above equation we arrive at the formula $D = \frac{d - d'}{td'}$. Using this method for determinations of the density of wax in the liquid state by a Westphal balance, Bulatkin[29] arrived at a cubical expansion figure of 0.0008138 per 1° (0.0004521 per 1° F) for one brand of petroleum ceresin known as "Petrosene A," and a figure of 0.0007911 per 1° (0.0004395 per 1° F) for another brand.

Hardness of Commercial Microcrystalline Waxes.

	Melting Point (°F)	Softening Point (°F)	Oil Content (%)	Durometer Hardness 34 °F	Durometer Hardness 84 °F
Petrowax	157–159	116–120	13	56	20
Petrosene A	167–171	139–144	7½	75	42
White Mineral	163–168	130–136	5	78	52
Pale Yellow	185–188	166–170	5–7	94	80

Penetration Indices of Microcrystalline Waxes. Penetrations are made on the microcrystalline waxes with a number 14 penetrometer needle (0.14 mm. diameter of the truncated blunt point), and a 100 gram top weight operating for 5 seconds, with the specimen at 25° (77° F). For very hard waxes a 200 gram top weight is used.

Specimen Labelled	Melting Point (A.S.T.M. drop) °C	Melting Point (A.S.T.M. drop) °F	Penetration Reading (No. 14, 100 g., 5 sec., 25°)
Amber 190/195	91	196	4.0
Steam Stripped 170/175	80	176	8.5
Cerese Yellow	77	171	12.5
Superla Light Yellow	79	174	11.5
Petrosene A (Yellow)	75	167	20.0
Be Square White	78	172	21.5
Amber 185/190	88	190	30.0
Petrowax	76	169	33.5

Miscellaneous Microcrystalline Waxes

Tank-Bottom Waxes. Tank-bottom wax is the wax from tank bottoms accumulated in the storage of the crude. Particularly suited for refining are certain grades of crude found in Eastern Texas. When the wax is dug out from the tank bottom, the product treated for the removal of water, and the light ends removed by distillation, the residue is a black wax of 180 to 185° melting point, of plastic consistency. This black wax contains up to 5 per cent of asphalt and in many respects resembles crude ozocerite wax. There is a market for this black wax, but a considerable quantity is refined to softer and harder grades of petroleum ceresins.

The black tank-bottom wax is acid treated to remove asphaltic compounds, bleached with suitable bleaching clay and filtered to an amber colored microcrystalline wax of 180 to 185° melting point. The tank bottom wax at this stage contains 10 to 15 per cent of oily hydrocarbons of high molecular weight. The latter can be removed by a benzene-acetone treatment if a more expensive, higher melting and less plastic, pale colored wax is desired. Waxes of the "tank bottom" type are also blended by some refineries with those of the "petrolatum" type to produce refined microcrystalline waxes of intermediate melting point range, and of the desired "fiber." As a whole tank-bottom waxes are not of equal quality to the petroleum ceresins, which are prepared from petrolatum stock by selective solvent adsorption.

"Be Square Waxes." The Bareco Oil Company at Tulsa, Oklahoma, refine microcrystalline waxes in different melting point ranges. These comprise brands known by the trade name "Be Square," of black, amber and white colors in both 170 to 175° F and 190 to 195° F melting point. The Be Square White waxes are both tasteless and odorless, and are considerably higher priced than the colored grades. The Be Square Amber ordinarily has an NPA color of 2, but paler colors are also produced.

A wax of the snow white microcrystalline type is more costly than the pale yellow, or amber type, because of the expense involved in the labor, and the loss of wax on filtering with relatively large volumes of clay.

Amorphous Block Paraffins. The term "amorphous block" paraffin is used here with some misgiving, for want of a better name, to describe microcrystalline paraffins that are not petrolatum waxes. They are not prepared from the long oil residuum of a fire or steam still, but are especially refined by-products of paraffin distillates, obtained from Pennsylvania and Mid-Continent crudes. They are marketed in soft to hard consistencies which have much flexibility. The soft wax is less soluble in butyl alcohol than in ethylene dichloride and is believed to be the ingredient which converts plates to needles, or needles to microscopic plates. These hydrocarbon waxes are pure white in color.

Henderson, Ferris and Cowles[12] realized the value of certain microcrystalline waxes remaining in the oil of crude scale wax on resweating in the processing of paraffin distillates; and the value of the oil passing from the wax in the first sweating, generally referred to as "foots oil." They were able to obtain excellent waxes by dewaxing a mixture of 75 parts of slack wax from Mid-Continent crude with 25 parts of petrolatum stock from a similar crude.

Henderson described the process as follows: "This oil-wax mixture was de-oiled by dissolving it at temperatures of the order of 50° in ethylene dichloride, using approximately 90 parts of the ethylene dichloride to ten parts of the mixture. The solution was then cooled to −15° and −10°, and the portion which crystallized out was again treated in the same way. This process was repeated until four re-crystallizations had been effected. The resulting material from the last of the four crystallizations, which was substantially oil-free wax, was fractionally distilled under an absolute pressure of approximately 10 mm of mercury, using steam, until 20 per cent bottoms remained. The fractions were collected, the first fraction containing 5 per cent of the total volume of the material subjected to distillation. Then five 15 per cent fractions, each of a successively higher boiling range than the one preceding, were collected. Each of the 15 per cent fractions was split by means of fractional re-crystallization from ethylene dichloride in the manner in which crystallization was previously effected." In this way a number of well defined waxes were formed ranging in melting point from 42° to 75°. Color improvement of the waxes was brought about by treatment with 18 pounds of fuming sulfuric acid per 100 pounds of wax at 15° to 25°; the acidity was neutralized with soda ash and the wax then filtered through clay.

Pennsylvania Micro Wax. A microcrystalline wax prepared by the Quaker State Oil Refining Corporation from Pennsylvania crude oil is a very tough, flexible, dry, and substantially oil-free wax of high tensile strength. Because of the difference in its crystalline structure as compared with regular paraffin waxes, it will bend and can be flexed while cool, without the crumbling or breaking away experienced when handling ordinary crystalline waxes.

Micro Wax has a melting point 63.3° (146° F) with a viscosity of 82 to 83 at 99° (210° F). It has a needle penetration of 22 units at 25° (77° F) by the A.S.T.M. method, excellent electrical insulation qualities, and strong adhesive characteristics. It is furnished in colors from white to amber. Micro Wax has very high oil absorptive qualities.

The following constants for Micro Wax are those listed by the refiner at Bradford, Pennsylvania.

Specifications

Matter insoluble in Benzol			0.1% Maximum
Saponification value			0.05 to 0.10
Corrosive properties			
(a) Reaction to Litmus			Neutral
(b) Reaction to Copper			None
Melting point—A.S.T.M. D-127-30			145°-146°
Flash Point—Cleveland Open Cup			500°-525° F
Fire Test			580°-595° F
Viscosity—at 210° F			75 - 85
Penetration—A.S.T.M. D-5-25			20 - 23
Specific Gravity at 34° (Solid)			0.890-0.900
Tensile Strength	Perkins Tester	—at 80°	220 # per sq in
Refractive Index	Sodium D Line		1.4450-1.4460
Tackiness Value	Bell Tel. Method		0.50-0.60

Electrical Tests

Tests at Radio Frequency of 1 Megacycle

Dielectric Constant	2.2
Power Factor	0.0002 or 0.02%
Loss Factor (2.2×0.0002)	0.00044

Tests at 60 Cycles

Dielectric Strength	510 volts/mil avg of 5 punctures

Tests on Direct Current

Volume Resistivity	over 600,000,000 megohm-cms

Note: The hydrocarbons in the high melting *paraffin block waxes* are normal straight chain saturated hydrocarbons, and have 2 molecules of the same kind, side by side, to the unit cell structure. For example, it is known that the hydrocarbon $C_{36}H_{72}$ is orthorhombic, with unit cell dimensions $a = 7.43$, $b = 4.97$, and $c = 46.2$ Å. U. (Angstrom units); and further that the CH_2 groups are spaced in the direction of the *c* axis at intervals of 1.27 Å. U., and that the other hydrocarbons follow the same pattern, although of different chain lengths. The *petroleum ceresin waxes* are of similar order, but with side chains twirled around here and there about the *c* axis, thus preventing the formation of large well defined plate or needle crystals. In a wax of the Micro Wax type the hydrocarbons are like those in paraffin, except that they appear to consist of unit cell structures in which the *dimers* comprise homologs of hydrocarbons differing in carbon content, thus interfering with the paraffin crystal pattern, and leading to a fine size of *mal* structure crystals, and a lower or depressed melting point despite the higher carbon content of the hydrocarbons. The behavior in the industrial applications of this wax differs from both the paraffins and the petroleum ceresins. Hence *Micro Wax* in the author's opinion should have a classification of its own, both from a chemical and technological standpoint.

Black Wax. Black wax is the name given to a "wax polymer" product obtained by blowing petrolatum, or waxes derived from petrolatum with air. The process requires controlled oxidation of wax-containing petroleum fractions, involving control of time, temperature, pressure, and volume of air. The finished product has a tremendously increased viscosity, a shining black color although the charging stock may be green, a somewhat increased melting point, and a very low acidity (0.1 mg KOH by A.S.T.M. test for neutralization value).

In the process of David[5] the charging stock is placed in a confined shell still, which has perforated pipes in the nature of a "steam spider" in the bottom of the still. Air under pressure is introduced through piping having an orifice meter interposed. The evolved gases are run off at the top through a line to a condenser and separated for by-product recovery. The charge is heated to about 450° F before the air blowing begins, the reaction being exothermic enough to maintain the temperature without further heating. The air is blown through the mass for about 48 hours. The viscosity rises rapidly after the first 24 hours of blowing. About 4000 to 5500 cubic feet of air per hour were used by David to obtain 3,659 gallons of *black wax* from 4,000 gallons of petrolatum. The black wax thus prepared had a melting point of 129° F, an open cup flash of 465° F, and a viscosity of 401 at 210° F Saybolt Universal contrasted with 101 for the charge. Black wax is suited for waterproofing and insulating.

Fybrene Wax. Fybrene Wax is the trade name given to a bleached, white, amorphoid hydrocarbon wax by its refiner. It has a melting point of 128 to 133° F, which is lower than the general run of microcrystalline waxes. Fybrene Wax flashes at 460 to 470° F; and has a Saybolt viscosity at 210° F of 50 to 55. It has a saponification value below 0.3. It is recommended for use in laminating compounds, since it is more pliable and decidedly more tacky than the softening agents customarily mixed with rosin. It is also recommended for blending with paraffin wax for the coating and impregnation of papers. Fybrene Wax is also employed in the manufacture of textile fiber products, cosmetics, pharmaceuticals, carbon paper, stencil paper and container linings. It is said to be of value as a film coating on the inside of collapsible tubes.

Bleaching of Petroleum Waxes

Bleaching of Hydrocarbons by Clay. Fuller's earth is a form of clay which is a natural, earthy, fine-grained material with a high capacity for decolorizing oils. It is composed of minerals that are hydrous magnesium aluminosilicates in their chemical composition. The name "fuller's earth" is derived from its first use, which was the removal of grease from woolen cloth in the process of "fulling" or "shrinking." Some clays are naturally active, such as fuller's earth; others are naturally inactive and develop their oil decolorizing ability only by treatment with acid. Bentonite is an example of the latter type; it is formed by the natural wetting of volcanic ash.

There are two processes used in decolorizing oils by clays, namely, (1) the percolation process and (2) the contact process. For the percolation process only fuller's earth is used, it is in granular (30–60 mesh) form in tanks which are 5 to 10 feet in diameter and from 20 to 30 feet high. After use clay must be cleaned with solvent; solvent is blown out by steam, the clay removed and fired at a high temperature to revivify it. In the contact process fine and coarse earth are mixed with the oil in a large vat, heat is applied, and after mixing the batch is placed in a filter press and the oil is squeezed from the clay. Acid-activated bentonites are used for the contact process.

The decolorizing efficiency of fuller's earth is greatly enhanced by the Hartshorne process. After the clay is mined, it is permitted to dry for a few days, and then crushed to coarse lumps. Thereafter it is dried in a rotary kiln to reduce the moisture to about 20 per cent, ground by grinding rolls, and screened to the various sizes. Hartshorne introduced three additional steps, namely (a) further grinding of the crushed lumps; (b) mixing of water with the ground earth, as in a pug mill; and (c) subjecting the earth to flow under high pressure, as in an extrusion apparatus. Subsequently the extruded earth is dried, ground, and sifted to the desired size. The extruding pressure at the extrusion die is about 500 pounds per square inch, and this disrupts the particles of the earth in such a manner as to greatly increase its decolorizing power.

A light green absorbent phyllite, named attapulgite, occurs at Montmorillon (Vienne, France) and Attapulgus, Georgia, (U.S.A.). Analyses of these clays are quite alike as shown below:

	SiO_2	Al_2O_3	Fe_2O_3	FeO	MgO	CaO	Na_2O	K_2O	H_2O
Montmorillonite	53.6	10.6	6.5	0.3	4.6	2.1	0.8	0.5	11.6
Attapulgite	53.7	9.3	3.6	0.2	9.6	1.2	0.9	0.5	9.7

It is suggested that attapulgite has been formed from an alkali-magnesian mica and that its absorbent properties are owing in part to zeolitic waters.

The clays are mined by the Floridin Co. in Northwest Florida, and by the Attapulgus Clay Co. at Attapulgus, Georgia; the deposits being about twenty miles from each other.

The principle of decolorizing paraffin or petrolatum waxes is the same as that for the lower hydrocarbons, except that heat must be maintained with the waxes to keep them in fluid state. The percolation process is the one commonly used for the hydrocarbon waxes.

The process of bleaching wax, as originally introduced by Weingaertner[30] consisted of heating the wax above its point of fusion to 130°, adding fuller's earth to the extent of 10 per cent, heating to 153 to 170°, and filtering.

Uses of Microcrystalline Petroleum Waxes

It has been estimated that about 180,000,000 pounds of microcrystalline waxes were refined in the United States in 1944. Many uses of these waxes are listed below:

- Adhesives for laminating
- Artificial fruits and flowers
- Barrel lining
- Belting impregnation
- Beer can lining
- Binding agents
- Blasting supplies
- Bottle cap liner coatings
- Brewers' pitch composition
- Candles
- Capsules
- Carbon papers
- Cheese coatings
- Chewing gum
- Collapsible tube lining
- Cosmetic creams
- Crayons
- Dental waxes
- Dressings for mechanical belts
- Drinking cups
- Egg preservatives
- Electrical insulation
- Electrotyping molding wax
- Field ration packages
- Floor wax
- Food wrappers
- Fruit coating
- Galvanized iron wire coating
- Glass fabric impregnation
- Grease and waterproof coatings
- Heat sealing compounds
- Honey comb foundations
- Laminants for paper, etc.
- Lining for acid pipe lines
- Lipsticks
- Meat coatings
- Metal drum lining
- Mildewproofing
- Ointments
- Ordnance packaging
- Paperboard cartons and drums
- Paper milk bottles
- Polishes
- Printing inks ingredient
- Radio parts
- Rain clothing
- Rubber compositions
- Rust preventatives
- Ship launching grease
- Shoe and leather treatments
- Soda straws
- Sound records
- Tank car treatment for wine, etc.
- Typewriter ribbon
- Vegetable coatings
- Wax acid bottles
- Wax emulsions and sizings
- Wax figures
- Wax toys
- Yarn lubricant for wool, etc.

Preventing Oxidation of Wax Melts

The prevention of oxidation of petroleum waxes when their melts are subjected to continuous heating must be considered in connection with certain specific uses. The hydrocarbons will oxidize and decompose sufficiently to yield measurable amounts of acids and esters; aldehydes and ketones are formed to a lesser degree, unless precaution is taken in handling the melts. Both surface and auto-oxidation can take place under conditions of industrial use. Decomposition is usually accompanied by the development of a slight acroleinic or burnt odor, a similar taste, and darkening of color when the wax is chilled. If the temperature of the melt is maintained at 50° F, or less, above the melting point of the wax, the oxidation is slight even over a duration of days of heating, provided the wax is being heated in a suitable vessel. At a temperature of about 100° F above the melting point, sufficient decomposition may set in during 24 hours in a glass vessel to yield traces of fatty acids, and a slightly reduced melting point. In 72 hours a titratable amount of fatty acid is evolved, and after a week's period the neutralization number and saponification value will be definite fractions of 1 per cent. There is less oxidation with a petroleum ceresin of low oil content than with a paraffin or ordinary petrolatum wax, under similar conditions of heating.

Concomitantly with the oxidation which takes place there is a lowering of the melting point which may approach 1° F in one day's heating of a microcrystalline wax at 250° in a non-metallic vessel. Oxidation takes place more readily in vessels made of brass, copper, zinc, and monel metal, and thus these metals should not be used for holding or contacting melted waxes. A petroleum ceresin heated at 250° F continuously over a period of 14 days in a copper vessel gave a saponification value of 0.75, contrasted with about one third that amount when a glass vessel was used. Aluminum is a desirable metal for a wax kettle as is also stainless steel. For pour-pans or molds, iron, aluminum, or tinned steel are generally used.

Antioxidants are occasionally added to waxes. These antioxidants include β-oxyanthraquinone, ditolylamines, gum benzoin, benzoic acid (sublimes at 100°), gum guaiac; citric acid, high molecular weight alcohols, and long chain hydrocarbons such as I.G. Wax Z. Several of these antioxidants are used only to the extent of 0.1 or 0.2 per cent to the batch. A wax which has been treated with silica gel is quite stable to oxidation. Surface oxidation as well as auto-oxidation can also be prevented by bubbling small quantities of CO_2 gas through the melt.

The effects of different conditions of exposure on the oxidation of S/V Petrosene A given below illustrate the oxidation characteristics of the micro-crystalline waxes.

Effect of Temperature (Heated in Glass for 24 Hours)*

Temperature	Color A.S.T.M.	Color Lovibond	Acid Number	Saponification Number
Original Wax	Lt. 2	5	0.00	0.00
200° F	2	5.5	0.00	0.00
250° F	Dk. 2½	8	0.05	0.30

Effect of Metal (Heated at 250° F for 24 Hours)*

Metal	Color A.S.T.M.	Color Lovibond	Acid Number	Saponification Number
Original Wax	Lt. 2	5	0.00	0.00
Iron	Dk. 3	8	0.06	0.74
Stainless Steel	Lt. 3½	14	0.03	0.56
Aluminum	Lt. 4½	25	0.03	1.80
Brass	Lt. 6	85	1.1	1.9
Copper	Dk. 8	175	1.2	3.1

*Determinations made by Socony-Vacuum Oil Co.

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Chapter 6

Synthetic Waxes and Wax Compounds

SYNTHETIC WAXES

Classification of Synthetic Waxes

The synthetic waxes may be divided into 11 groups, as follows:

(1) Chemically synthesized compounds that have no close relation to the natural waxes in chemical structure, but which are similar to them in physical characteristics. These compounds are the *phthalimides*; polymers of ethylene oxide like *Carbowax*; terphenyls like *Santowax*; and others.

(2) Halogenated straight chain hydrocarbons, *e.g.*, the chlorinated paraffin waxes, and the chloro-paraffin cyclic condensation waxes, such as *Halowax*.

(3) Unsaponifiable waxes prepared by heating a natural ester-wax or high molecular-weight waxy ester, with a catalytic agent to remove carboxyl (CO_2) groups, so as to form high molecular-weight hydrocarbons and alcohols; the decarboxylated product is then directly hydrogenated to obtain the end product. *E.g.*, some of the *I. G. Waxes.*

(4) Emulsifiable wax-like solids produced by esterifying a liquid polyhydric alcohol with a higher fatty acid by means of heat and a catalyst, and then purifying the solid reaction mass. *E.g.*, *diglycol stearate.*

(5) Synthetic hydrocarbon waxes prepared by a water-gas synthesis in which carbon monoxide (CO) is reduced under pressure by means of a catalytic agent. *E.g.*, the waxes made by a modification of the Fischer-Tropsch synthesis.

(6) Hydrogenated waxes produced by the optimum hydrogenation of drying oils, or by reacting a hydroxy acid produced by the hydrogenation of a non-drying vegetable oil with a wax alcohol to produce natural-wax-like esters. *E.g.*, hard wax-like products such as *Opalwax.*

(7) Symmetrical ketones produced by the catalytic treatment of the higher fatty acids. *E.g.*, *palmitone, stearone.*

(8) Unsymmetrical ketones prepared by the Friedel-Crafts condensation of fatty acids and the like with cyclic hydrocarbons. *E.g.*, wax-like end products such as *furyl heptadecyl ketone,* and *phenoxyphenyl heptadecyl ketone.*

(9) Amides or imide condensation derivatives of saturated fatty acids having 12 to 18 or more carbon atoms. *E.g.*, *Armorwax.*

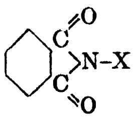
(10) Synthetic branched chain hydrocarbons prepared by ketonizing fat acids from fish oils, and then hydrogenating the ketones. *E.g.*, *synthetic ozocerite.*

(11) Polymerized ether waxes produced by the treatment of a fatty alcohol by adsorption of an alkine gaseous hydrocarbon to obtain an ether monomer which is then polymerized. *E.g.*, *I.G. Wax V.*

The synthetic waxes are waxes only in the sense that they possess physical properties customarily attributed to the natural waxes. The science involved in developing waxes that duplicate the natural waxes in chemical composition has progressed slowly indeed. Improvement in the art of oxidizing the paraffins to acids with the same carbon content, and then combining these wax acids with alcohols of a high molecular weight, would be the means of yielding the types of esters that are found in the natural waxes. The source of the wax alcohols would be derived from the reduction of mixed fatty acids by means of hydrogen with the aid of a catalyst. In some instances where the artificial esters are compounded with small amounts of free wax acids and alcohols as well as hydrocarbons, the resultant artificial wax would be difficult to distinguish from the natural wax of similar composition.

The synthetic waxes that are on the market to-day are for the most part produced by patented processes, and their names are registered trade-names. Many of these trade names have become so familiar to the wax technologist that they are regarded as indispensible, and are continually referred to in technical publications as components in recipes that call for wax material. Examples of such waxes are *I. G. Wax OP*, *Opal Wax*, *Halowax*, and *Lanette Wax.*

Phthalimides. High molecular weight phthalimides of the general formula



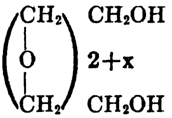
wherein X is a straight chain hydrocarbon radical having six or more carbon atoms have been found by Pool and Harwood,[17] to be very wax-like. They give an extremely high luster when polished, and when dissolved in a suitable solvent make an excellent waxing and polishing composition.

The phthalimides can be prepared by heating 1 mole of phthalic anhydride with 1 mole of a primary aliphatic amine until the evolution of water ceases; *e.g.*, 185 grams of dodecylamine and 148 grams of phthalic anhydride are mixed in an open flask and then heated to 165° for a period of four hours, at the end of which time the evolution of water ceases. The present *N*-dodecyl phthalimide is poured into molds and allowed to solidify. It is a medium hard, light colored wax, and melts at 65° to 67°. The *N*-octadecyl phthalimide melts at 80° to 81°, and the phthalimide which is a mixture of *N*-tetradecyl, hexadecyl, and octadecyl phthalimide has a melting point of 55° to 57°.

Sometimes the phthalimide wax is used with *carnauba wax*, 50 : 50, and the mixture is emulsified for waxing and polishing compositions. In other instances the waxes are mixed with a solvent to make polishing paste.

Carbowax. Carbowax is a synthetic chemical product which has the physical appearance of a wax. It is, however, not a true wax in its chemical structure, nor in its physical performance. It is not generally miscible with either the true waxes or paraffins, but it is of value when used in conjunction with the so-called "emulsifiable waxes," and in other ways. It is compatible with resins but not with oils or gums. Carbowax is the trade name given to the aforesaid material by the Carbide and Carbon Chemicals Corporation. Its composition has been disclosed by McClelland and Bateman[16] as consisting of one or more of the higher polyethylene glycols. The commercial Carbowax compounds are all mixtures of several polymers, and are rated according to their mean molecular weights, such as 1000, 1500, 1540, 4000, and 6000, the last being the newest of the series.

Carbowax has the following general formula:



$$\left(\begin{array}{c} CH_2 \\ | \\ O \\ | \\ CH_2 \end{array}\right)_{2+x} \begin{array}{l} CH_2OH \\ \\ \\ \\ CH_2OH \end{array}$$

Carbowax is supplied by its manufacturer in several grades from soft to hard.

Carbowax Compound 1500 is a blend of a polyethylene glycol of 300 molecular weight and Carbowax 1540, and has an average molecular weight between 500 and 600. It is a bland, odorless, water-white solid with the consistency of a low melting petrolatum. It has a specific gravity at 20°/20° of 1.150, a flash point of 430°, and a Saybolt viscosity at 210° F of 60 to 90 seconds. It is 60 to 90 per cent soluble in water at 20°, and has 30 per cent of the hygroscopic power of glycerol. Carbowax 1500 is particularly suited for use in bases and vehicles of cosmetics. It is suited as a base for carrying medicaments in pharmaceutical ointments. A technical grade is used as a lubricant for rubber molds.

Carbowax 1540 has the appearance of paraffin. It differs from Carbowax 1500 in viscosity and in hygroscopicity. It has a Saybolt viscosity of

100 to 150 seconds at 210° F, and about 5 per cent of the hygroscopic power of glycerol. In contrast with complete water solubility is its unexpected solubility in aromatic hydrocarbons such as benzol and toluol. The Carbowaxes are also soluble in acetone, ethanol, Cellosolve, ethyl acetate, but almost insoluble in straight-chain hydrocarbon liquids.

Carbowax 1500 offers possibilities as a plasticizer in casein, gelatine, and glue adhesives in sizes, binding agents, textile and paper softeners, lubricants, and preservatives. It can be used as a scrubbing liquid for air purification, in the formulation of belt dressings, and for cosmetics, lotions, and hair preparations. Carbowax 4000 is of special interest to manufacturers of water paints, calsomines, shoe dressings, and sizing materials. It can be used to advantage in water-soluble crayons for artists, in marking textiles when mark must later be eliminated, in etching-fluids, and whenever it is desirable to have an excellent surface tension depressant. Carbowax 4000 has a viscosity of about 600 Saybolt seconds at 210° F. Carbowax 6000 is about ten times as viscous. Both of these Carbowaxes are available commercially in flake or chip form.

Among the applications which have been developed for Carbowax are nail polish, shoe polish, remover cream, mold lubricants for rubber and viscose rayon. It can also be used as a substitute for glycerine in toilet goods preparations. According to a report published under a fellowship at the Mellon Institute, Carbowax is comparatively non-toxic. It costs about twice as much as propylene glycol.

Ethylene Oxide Polymer. In a British patent of Imp. Chem. Ind., Ltd.,[16b] ethylene is converted into a solid wax-like body when subjected to very high pressure (at least 500 atmospheres) and a temperature of 100 to 400°, in the presence of other unsaturated compounds and a polymerization catalyst such as a small quantity of oxygen or benzoyl peroxide. The patent includes the polymerization of other unsaturated compounds to yield products that are not waxes, but are otherwise useful to industry. The extruded products include films, threads, tubes, rods, and sheets.

Santowaxes. The Santowaxes are synthetic hydrocarbon waxes, the composition of which has not yet been disclosed. Some students believe that they have a terphenyl structure, *i.e.*, *ortho*-, *meta*-, and *para*-diphenyl benzene, or mixtures of these or allied derivatives. The Santowaxes are offered in the market as *O*, *M*, *P*, and *R Santowax*, by the Monsanto Chemical Co., St. Louis, Mo. The *ortho* (*O*) type is yellow in color; density 1.097 grams per cc; solidifies at 140°, with a second hold point at 56°; distils at 336 to 402°; almost insoluble in alcohol; soluble to the extent of 5 per cent in cold benzene; soluble in warm fuel oil or turpentine; soluble in chlorobenzene; coefficient of thermal expansion 8.3×10^{-4} at 25 to 60°. It is soft after melting but hardens completely 40 hours after melting until it is comparable with montan wax in hardness. *Santowax M* is microcrystalline, will become as hard as candelilla wax, and is very stable to heat. *Santowax P* is a nearly white crystalline hydrocarbon, very stable to heat, and with a very high but unstable melting point; the solidification point is 209 to 213°.

Santowaxes have been suggested for use in the manufacture of rust-inhibitive coatings for steels; in impregnating compositions for waterproofing paper and strawboard material; in sealing compounds, wax finishes, anti-fouling and fire retardant resinous paints; and for other purposes.

Aerosol OT. Aerosol is the trade name given by the American Cyanamid Company to the dialkyl alkaline salts of sulfosuccinic acid, that characteristically are *wetting agents*. *E.g.*, "Aerosol OT" is *dioctyl sodium sulfosuccinate*. It resembles white slack wax in appearance and consistency, except that it is marketed in extruded pellet form. Aerosol OT has a molecular weight of 444; has a slightly camphoraceous odor and taste; is somewhat hygroscopic; is dispersible in warm water; and soluble in most polar and nonpolar solvents, and in warm oils, fats and resins when heated to 75°; it is not directly miscible with hydrocarbon waxes but mixes well with beeswax and most of the vegetable waxes. "Aerosol M.A." is chemically known as *dihexyl sodium sulfosuccinate*, and is less soluble than the dioctyl compound in organic liquids, but dissolves readily in hot water. Both act as good wetting agents in formulations of floor waxes, in washing photographic prints, and in the dental laboratory for wetting wax investments in order to prevent the formation of bubbles with consequent imperfections during the casting of the plaster.

Acrawax. Acrawax C is the name given to a synthetic wax of unusually high melting point manufactured by the Glycol Products Company, New York. Acrawax C is a hard wax, light tan in color, and of high luster. The composition of the wax has not been disclosed. Some students believe that its chemical structure is a condensation of a cyclic imide and a higher fatty acid.

Acrawax C has a melting point of 137 to 140°, (278.6 to 284° F); flash point 285° (open cup); specific gravity 0.975 at 25°/25°, 0.830 at 141°; moisture absorption (48 hours at 100 per cent R. H.) 0.6 per cent at 35.5°; and 428 volts per million dielectric resistance. It is insoluble in water, insoluble in alcohol, completely soluble when molten in naphtha, toluene, and turpentine and gels from the latter on cooling. Its behavior with *ortho*-dichlorbenzene is similar to that with turpentine. Acrawax C has been listed as compatible (ratio 1 : 1) with asphalt, candelilla wax, carnauba wax, microcrystalline wax, paraffin, stearic acid, and several resins.

Numerous uses for Acrawax C have been suggested by its manufacturer; namely, in adhesives of the thermoplastic heat-sealing type; in asphalt to raise the softening point; in carbon papers to dissolve dye, *e.g.* crystal violet; in electrical insulation compounds; in powdered forms as a lubricant for thermosetting plastics; in steam pressure mechanical packings; in paper coatings when blended with other waxes; in plastics; in polishes when blended with other waxes; in rubber stocks to prevent blooming, or to prevent tack in synthetic rubbers; as a mold lubricant for sintered bearings; as a protective coating on welding electrodes; and in varnishes and lacquers to increase salt spray resistance.

Armorwax. A synthetic wax quite similar in melting point and other properties to Acrawax C is *Armorwax,* the trade name given to a recent product of Armour and Company. The melting point of Armorwax is 135° (275° F). In blending with paraffin the Armorwax is best melted first, not too highly and the paraffin added slowly. The paraffin when in excess becomes the solvent and the *Armorwax* the solute, depressing the crystallization of paraffin on congealing. Small quantities such as 5 per cent greatly elevate the melting points of both paraffin and beeswax, whereas the effect on stearic acid is negligible. Armorwax has a light tan color, is insoluble in water, but soluble when melted in many of the polar and nonpolar solvents, and has a tendency to gel on cooling. It is useful as an ingredient in shoe pastes and floor polishes, for sound records, protective coatings, carbon papers, etc.

Chlorinated Paraffin

Chlorinated paraffin, or *chloro-paraffin* as it is also called, is a chemical which in consistency may be liquid, semi-fluid, or solid, depending upon the type of paraffin chlorinated and the degree of chlorination. Each H atom of the terminal CH_3 groups of the paraffin as it is replaced by a Cl atom increases the chlorine content of the end product by 11 per cent, a trifle more or less, so that the chloro-products have 11, 22, 33, 44 per cent or even higher of chlorine. The commercial demand is for a chloro-paraffin of not less than 30 per cent chlorine. Ordinarily this chloro-paraffin is a somewhat reddish fluid, miscible in all proportions with castor oil, and will act as a stabilizer and agent in bringing about compatibility of castor with mineral oils in the field of lubrication. It is termed a *solubilizer*. It also has excellent *dielectric* properties.

Chloro-paraffin is prepared by one of two methods: (1) The Bolley method* in which the chlorine is passed through melted paraffin until the desired Cl content is reached; hydrogen chloride is evolved as a by-product. *E.g.*, *slop wax* can be easily chlorinated by the Bolley method. (2) The Bohringer process[2], patented in 1910, in which chlorine is conducted into

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[*] Ann., 106, 230 (1858).

the solution or suspension of the material, in carbon tetrachloride (CCl_4), until the resultant product contains at least 30 per cent of chlorine. Chlorination can thus be carried out at a low temperature and pressure, using the actinic rays of the sun as an activating agent. Solid products, water white in color, and transparent can be obtained when the CCl_4 is recovered.

Chlorinated products can be made from paraffin, mineral, montan and vegetable waxes, in which energetic chlorination is effected wholly, or partially in the presence of catalysts. *E.g., flax wax* can be chlorinated to a 36.2 per cent chlorine content. The olefins can be chlorinated highly, to a Cl content of more than 70 per cent. Many useful NH_2, OH, and SO_3H derivatives can be prepared from the chloro-paraffins.

Chlorinated paraffin is a colorless to amber colored viscous liquid. It is marketed in 55-gallon drums containing 525 pounds, and in tank cars. Because of its splendid fire-retardant, mould-proofing, and water-repellent properties it has been used extensively for proofing tent canvas. It is a plasticizer for chlorinated rubber and proofing paint. It is used in extreme pressure lubricants (Lubricol Sales Corp., Cleveland, Ohio). Chlorinated paraffin is used in very small quantity in lubricants by many oil refiners. It is listed as a plasticizer for vinylite resins, nitrocellulose, polystyrene, methacrylates, coumarone indene, and other resins. Solutions of chlorinated paraffin in aromatic solvent (not mineral spirit) can be advantageously fortified by the addition of some more highly chlorinated body such as chloropropane.

Chloropane Wax 130. This is an octachloropropane of a waxy structure resembling paraffin in appearance. It is a tough white crystalline wax possessing a mild camphor-like odor. It is insoluble in water, soluble in alcohol, ether, and most chlorinated solvents. Its manufacturers, the Hooker Electrochemical Company, have given it the empirical formula $C_3H_{0.15}Cl_{7.85}$ with a molecular weight of 311, constituting about 85 per cent octachloropropane, and 15 per cent heptachloropropane (1,1,1,2,2,3,3). It has a melting point range of 110 to 135°, with last crystal point at 130 to 135°, it boils at 210 to 270° at 760 mm pressure. It is compatible as a plasticizer with resins such as polyvinyl chloride, vinylite, styrene, urea formaldehyde, Piccolyte, phenol formaldehyde and methacrylates, as well as with rubber and certain rubber substitutes. Among suggested uses are the following: plasticizer, dielectric wax, ingredient in pyrotechnic compositions, chemically resistant lubricant.

Chlorowax. Chlorowax is the name given to a highly chlorinated paraffin (69.7 per cent Cl) made by the Diamond Alkali Co. The product as it appears on the market, is a brittle, pulverized, water-insoluble resin and not a wax. Chlorowax melts at 90° (ball and ring method) and has a specific gravity of 1.64. It starts to decompose below its ignition point.

In blending it with other ingredients care must be taken so that a temperaature of 130° is not exceeded. Chlorowax is of value as a flame retardant for protective coatings. A more highly chlorinated paraffin is that of the Hooker Chemical Co., which contains 76 to 78 per cent of chlorine. This is a pale-colored, brittle resin, softening at 100°, and used in paints to help them withstand severe weather conditions.

Chloro-Wax Cyclic Condensation Products

Chlorinated paraffins may be condensed with naphthalene and the latter chlorinated, or with naphthalene already chlorinated, to produce hard waxes that have fire-retardant, electrical-insulating, and chemical-resistant properties. Of this description are the *Halowaxes* and *Seekay Waxes*, which differ only in the manner in which the chlorination has been carried out, the type of catalyst employed, and the flexibility of the resultant product. These products are obtained by chlorinating paraffins and condensing them with a double ring aromatic hydrocarbon, such as naphthalene, in the presence of a catalytic agent, aluminum chloride.

Similar condensation products are of value as pour-point depressants for lubricating oils. In the process of Davis[4] the specification calls for a paraffin of 120 to 130° F melting point, of molecular weight about 300; the wax is melted and heated to about 200° F, then the chlorine bubbled through it until 12 to 14 per cent is absorbed. The chlorinated paraffin is condensed with naphthalene using aluminum chloride as a reactor, the free HCl being expelled in the heat reaction to produce the end product. In the process of Reiff[20] the chlorinated paraffin is condensed with phenol, also using aluminum chloride as the reactor, heating the reactants, and expelling the HCl. If 3 per cent of aluminum chloride are used and the temperature is raised to 350° F, the resultant product is a wax-substituted aluminum phenate, which can be hydrolyzed to form the desired wax-substituted phenol. The pour-point depressant is then referred to as a pure *poly-wax-substituted phenol.*

Frolich[8] has prepared a condensation product similar to Halowax by reacting chlorinated paraffin with naphthenic acid. For example, 100 cc of chlorinated paraffin (11 per cent chlorine strength) were placed in a flask with 100 grams of naphthenic acid. The contents were heated to 130° F, and mechanically stirred. To this mixture 50 grams of aluminum chloride were then added over a period of one-half hour, and the temperature was slowly raised to 300° F, and maintained at that temperature until the end of the reaction period—about five hours. During this reaction hydrochloric acid was evolved and removed from the flask. When the reaction period was over the flask was cooled to about 125° F and its contents diluted with 1000 cc of kerosene and then neutralized by adding water and alcohol to hydrolyze the catalyst. The kerosene extract separated from the aqueous and sludge layer was withdrawn, and distilled with fire and steam to a temperature of 600° F to recover the wax modifying agent as a residue. The product had a Saybolt viscosity of 990 seconds at 130° F, 186 seconds at 210° F; it had an acid value of 4.3 and a saponification value of 8.3. The yield was about 40.5 per cent of optimum. When 5 per cent of this product was added to a waxy oil having a pour point of 30° F, it was found that the pour point was reduced to + 5° F.

By using 100 grams instead of 50 grams of the aluminum chloride, a similar but more effective product was obtained. It required 1 per cent to reduce the pour point from 30° F to + 15° F, while 5 per cent reduced the pour point of the same oil to − 5° F.

Halowax. Halowax is a hard, tough, pale yellow synthetic wax having a chemical odor, more or less like chlorine, possessing peculiar chemical and physical properties. There are several grades of Halowax: (1) a hard crystalline solid, white to pale yellow in color; (2) a hard semi-amorphous solid of pale yellow color; and (3) a tough amorphous solid of the same color. The specific gravities of these waxes at 15° are 1.560, 1.680, and 1.780 respectively. The melting points range between 65° and 130°, the boiling points between 550° and 700° F, and the flash points between 284° and 392° F. The waxes do not support combustion so there is no fire point. The acid number is about 0.1. The coefficients of linear expansion range between 0.00008 and 0.00005 respectively for the solid waxes.

The Halowaxes are high in dielectric strength and have an extraordinary specific inductive capacity (4.5 to 5.5). They are neutral and non-corrosive to metals, are very moisture repellent, and melt to a liquid of low viscosity. These properties make them of great value in the electrical industry.

Halowax is widely used to protect fibrous materials from fire hazard, particularly in the insulation of electrical wires. Halowax is employed in compounding many types of liquid, paste, and emulsified polishes. It aids in the bleaching of other darker colored waxes. It is, however, not practicable for any purpose relating to food packaging except in extremely small quantities in a wax composition, since it emits an objectionable aromatic odor. Flexible protective coatings can be made with chlorowaxes blended with petrolatum waxes.

Dodd's Chloro-Wax Blend. A fire resistant composition for the sealing of electrical apparatus can be prepared from chlorinated naphthalene and a bituminous or wax-like product. A particularly suitable composition has been given by Dodd[4b] in which chlorinated naphthalene (54 per cent Cl_2) is melted with a smaller amount of chlorinated paraffin wax (53 per cent Cl_2), oleic acid and petroleum jelly and hexachloroethane thoroughly stirred into the mixture, the temperature being maintained at 100°. Lime, which reacts with the oleic acid, and finally china clay are added to the melt with stirring. The mass is then allowed to cool, and masticated on rolls to a completely homogeneous paste or putty, which can be colored if desired. A typical formula is chlorinated naphthalene 29.1, chlorinated paraffin wax 9.0, oleic acid 6.5, petroleum jelly 5.2, slaked lime 3.2, hexachloroethane 1.3, and china clay 45.7 parts.

Seekay Waxes. The Seekay Waxes are chlorinated naphthalenes manufactured by the Imperial Chemical Industries, Ltd., in England. They resemble natural waxes in appearance and also in their water-resisting properties, inertness to chemicals and good electrical insulation properties. In addition they have two important advantages: (a) they are non-inflammable, and (b) they can be obtained with melting point as high as 125°. The waxes have definite insecticidal and fungicidal properties.

In color the Seekay Waxes vary from dark brown or black brown to pale yellow. Grades are available in melting points of 65 to 70°, 90 to 95°, 110 to 115°, and 120 to 125°. They boil at 1 mm pressure at 143 to 190° (290 to 375° F). The specific gravity at 15° is 1.550; specific heat at 18° is 0.202, at 110 to 120° is 0.278; specific inductive capacity 5.4. They have a slight odor. The waxes are very soluble in dichloro- or trichloroethylene, benzene, ethyl ether, acetone, but are less soluble in amyl alcohol or methanol. They are compatible with bitumens.

Seekay Waxes are useful for waterproofing, flameproofing, electrical insulation, insecticides, fungicides, and wax or bitumen blending.

Chlorinated naphthalenes must be handled with care and overheating should be avoided as the fumes or dust of these waxes are toxic to the skin.

I. G. Waxes

I. G. Waxes are synthetic products prepared from natural waxes as basic raw material. The addition of I. G. Waxes in very small quantity will often improve other waxes in melting point, luster, hardness, solvent absorption, or in other ways, depending upon which type of I. G. Wax is added. I. G. Waxes have been used extensively in the arts and industries.

It was found by Jahrstorfer of the I. G. Farbenindustrie Aktien-gesellschaft, Frankfort-on-the-Main, Germany, that the aliphatic acyl compounds of bleached montan wax could be linked together in an ester-like fashion by converting the free carboxyl (COOH) group of the free acids into other groups containing the —CO— linkage, which do not contain a carboxyl hydrogen atom, as for example ketones, anhydrides, and the like. This condensing—splitting action can be effected by means of heating the wax with a suitable catalyzer. Later Jahrstorfer found that it is frequently an advantage to subject the products simultaneously or subsequently to a hydrogenating treatment.

I. G. Waxes, which have been replacing carnauba wax in the production of leather polishes and creams, according to Hamor[1c] are made from purified montan wax, by esterifying or otherwise altering the COOH group of the high molecular weight aliphatic carboxylic acids comprising it. The *montanic acid* which constitutes almost 90 per cent of refined montan wax, exists very largely in a free condition, and can be esterfied readily to an ester with an extremely long carbon chain. The resultant effect is to produce a wax of very high melting point and of other unique properties.

High molecular wax-like substances produced from high molecular compounds of oils and waxes containing a carboxyl (COOH) group when treated catalytically so as to split off CO_2, and then hydrogenating the resultant product, will according to Jahrstorfer[14] provide substances good for dressing and impregnating all kinds of fiber, paper, etc. In splitting off the CO_2 group from the COOH containing wax, the powdered catalyst, such as nickel, iron, tungsten sulfide, or alumina is spread on a carrier—like silica, silica gel, kieselguhr, activated carbon—and mixed with the wax. The hydrogen treatment is conducted under pressure in the presence of the catalyst at a temperature of 180 to 200°. Pungs and Jahrstorfer[18] state that the properties of natural waxes can be improved by treatment with hydrogen at 100 to 150 atmospheres of pressure and 200° plus temperature in the presence of a cobalt or nickel catalyst.

In the Jahrstorfer and Schwarte[14a] patent, the inventors give several specifications for the preparation of I. G. Waxes. In one example 1000 parts of brown-colored montan wax are heated for 12 hours to 310° while stirring with 200 parts of kieselguhr and 30 parts of iron powder. After filtering off the catalyst the wax has a melting point of 100° which contrasts with 83° for the montan wax. By catalytic hydrogenation of this product at 300 atmospheres and 250° with a catalyst made by applying 20 parts of nickel to 80 parts of kieselguhr, a pure colorless hard product is obtained having the following characteristics: melting point 104°, acid value 0, saponification value 0, hydroxyl value 2. This product is therefore practically a pure hydrocarbon of high melting point. This is probably identical to the product marketed in America by the I. G. industry, under the name of *I. G. Wax Z.* It is interesting to note that the acid value (107) and the saponification value (143) of the montan wax are brought down to 0 in the production of I. G. Wax Z.

It had been known prior to the aforesaid German patents that the montanic acids (C_{28}, or C_{27}–C_{29} mixtures) probably originate as the result of the oxidization of the hydrocarbons in the liquate (see montan wax, p. 203), while the montanic alcohols are formed by the reduction of the corresponding acids under high pressure. The two when chemically combined will produce *montanyl montanate* and closely associated esters. *Montanic acid* under the influence of heat will readily combine with hydroxy acids such as ricinoleic, $C_{18}H_{34}O_3$, an abundant constituent of castor oil, to produce a high ester wax. Bleached montan wax can be combined with cocoanut oil fatty acids and ethylene glycol by means of heat to produce a high melting wax.

German I. G. Wax Process and Equipment. The useful source of montan wax in Germany is the brown coal of 10–18 per cent wax content at Halle Riebeck where there is an extraction plant for raw wax. Finely pulverized brown coal is dried in a pipe drier with steam heat at 150–180° to a moisture content of 10–12 per cent. The dried coal is then sieved to free it from dust, and extracted by a Soxhlet type of extractor with a mixture of 80–85 per cent benzene and 15–20 per cent of crude wood alcohol. The extract is evaporated, the solvent distilled and recovered, leaving the crude montan wax, which is then steam distilled to remove the last trace of solvent. It contains about 70 per cent wax, 15 per cent resin and 15 per cent bitumen. The residue in the extractor is briquetted with pitch or tar and sold as a fuel.

The crude wax is made by the Rebeck'sche Montan Werke at the Amsdorf and Wansleben plants,[5a] both near Halle. It is either deresinified with alcohol and distilled at their Volpke plant at Kreis Neubaldensleben, near Magdeburg, to produce the montan wax of commerce, with oil and pitch as by-products; or, more completely extracted with a benzene-alcohol mixture to produce a 95 per cent wax suitable for conversion to the so-called I. G. waxes at Oppau and Gersthofen, by the I. G. Farben A. G. At Amsdorf the crude wax is milled to a powder which is wetted with alcohol to prevent explosions. The powder is then heated in a vessel to 40–45° and agitated with the mixed solvent. The resin rises to the top of the vessel where it is removed. This resin liquid is further agitated to settle out the wax. The combined fraction is heated with steam outside as well as inside of the vessel to remove all of the residual solvent. The by-product resin is sold as a rosin substitute or blended with raw wax and sold to the leather industry for leather impregnation. The deresinified wax is oxidized with chromic acid-sulfuric acid solutions at the oxidation plant at Gersthofen, to produce *I. G. Wax S.* [The ketone and paraffin plant at Oppau was destroyed by bombing in World War II; the fatty acid and ester plant at Gersthofen is intact.]

The oxidation plant at Gersthofen consists of a series of lead lined cast iron kettles, jacketed and lagged, each suited to treating a ton batch of wax. The kettles can be cooled by water or heated by steam, and are fitted with agitators and bottom outlet. The vessels for holding the acid solutions are situated on a staging above the oxidation kettles, and the oxidant and spent liquor are handled in lead pipes on wooden guttering. The oxidation is carried out in batches and in three stages[9a]; the first is exothermic but can be controlled without external cooling by adding the oxidant slowly over a period of 4 hours to the molten wax with agitation. In the second and third stages additional steam heating is employed, with a temperature of oxidation of 110–120°, each stage taking 3 hours to complete, and half an hour to separate spent acid, although it is possible to work a counter current oxidation process with a battery of reaction vessels. The composition of oxidizing liquor is 1 part CrO_3 plus 3 to 4 parts H_2SO_4, and the amount of CrO_3 necessary to each batch is not less than $1\frac{1}{4}$ parts to 1 part of wax. The spent liquors are regenerated electrolytically. The product is now treated in another vessel with sulfuric acid to remove chromium complexes, and then with water to remove the sulfuric acid, and the water removed with the aid of heat under slight vacuum. The molten wax is run off into aluminum trays where it is congealed and the hard wax, *I. G. Wax S*, broken up by hand. It can be flaked or milled.

Composition of Specific I. G. Waxes.[5a] *I. G. Wax OP* is a mixture of the 1:3 butylene glycol ester and the calcium salt of I. G. Wax S. The ester itself is of little practicable use.

I. G. Wax E is a glycol ester of I. G. Wax S containing a slight excess of the latter. It is prepared from heating together I. G. Wax S 2000, ethylene glycol 200, and sulfuric acid 0.2 parts. The molten mixture is agitated for 10 to 12 hours at 120°.

I. G. Wax S, the manufacture of which has been described, consists essentially of 85 per cent of a mixture of C_{26} to C_{30} wax acids (montanic acid from the hydrolysis of the original esters, monobasic acids from the oxidation of the wax alcohols split off during hydrolysis and about 20 per cent of dibasic acids from $-OH$-containing esters) and 15 per cent of unreacted esters. A similar product made by a milder oxidation of the extracted montan wax is *I. G. Wax L*, which contains a little more of the unreacted esters.

I. G. Wax BJ is a mixture of the ethylene glycol esters of equimolecular proportions of I. G. Wax S and other fatty acids such as stearic and palmitic, modified by the addition of soft paraffin wax.

I. G. Wax V is not a montan wax product but a polymer of the octadecyl ether of vinyl alcohol, $C_{17}H_{34}CH_2\cdot O\cdot CH : CH\cdot OH$. It is prepared by reacting octadecyl alcohol (derived from sperm oil) with acetylene, distilling the ether, and polymerizing the monomer with the aid of boron trifluoride.

I. G. Wax Z is a microcrystalline hydrocarbon of 55 carbon chain length, which was manufactured at Oppau by ketonizing I. G. Wax S, or I. G.

Wax L., or both, and then reducing the ketone with hydrogen to the hydrocarbon in accordance with the Jahrstorfer process. This process was carried out by heating the base wax at 300° with 1 to 2 per cent of metallic iron powder (prepared from iron carbonyl) in a closed vessel; the pressure inside the vessel is kept down to 3–5 atmospheres by blowing off the excess CO_2 and H_2O formed, during the processing time of 30 hours. The ketone is then reduced at 200 atmospheres of pressure with hydrogen in the presence of a metallic nickel catalyst at 350 to 380°.

I. G. Wax OZK is an imitation of ozocerite. It was made at Oppau by an undisclosed method. It is believed to have been produced by hydrogenating ketones prepared from the fatty acids derived by the hydrolysis of marine oils, such as sperm oil. It consists of hydrocarbons of a smaller chain length than I. G. Wax Z. Its density at 4° is 0.911.

Other I. G. Waxes exist but are of less importance than those referred to above.

Properties and Uses of I. G. Waxes. The physical properties of I. G. Waxes are given below. Much of this information has been obtained through the General Dyestuff Corporation.

Brand	Melting Point (°C)	Melting Point (°F)	Acid Value	Ester Value	Color
OP	105–108	221–226	10–15	110–125	light yellow
E	80–83	176–181	15–20	140–155	light yellow
S	82–84	180–183	142–152	25–35	very pale yellow
B (bleached)	75–77	167–171	50–60	125–135	very pale yellow
B (unbleached)	75–77	167–171	10–20	130–150	light brown
V	50	122	0	10	snow white
Z	101–103	214–217	0	0	snow white
OZK	75–77	168–172	0	0	snow white

I. G. Waxes OP, E, S, and Z are of particularly high degree of hardness, the OP being the hardest. I. G. Wax OP and I. G. Wax Z have exceptionally high melting points. OP has an exceptionally high capacity for binding oils.

I. G. Wax OP is essentially a high molecular ester wax. It has a specific gravity of 1.0400 at 25°, 1.0298 at 35°, 0.863 at 118, and 0.857 at 127°. In carbon tetrachloride, ethyl acetate, amyl acetate, butyl acetate, benzene, toluene, xylene, benzine, varnoline, trichloroethylene, and turpentine the I. G. Wax OP may be dissolved hot, and on cooling a jelly like mass is obtained in which the solvent is bound to the wax. The OP Wax melts easily when heated in mineral oils or in vegetable fats, and will thicken in consistency of such oils or fats. OP wax when used in floor wax and in shoe cream produces a high durable gloss. The oil uptake of OP wax was shown by Lux[15c] in 1935. He took as his standard a solution of 22 parts of 75° refined ozocerite and 78 parts of turpentine. The oil uptake was the number of parts of solvent required to make a paste of standard consistency as determined at 20° with a flat surface sinker. The number of parts of solvent per 100 parts of wax required was: ozocerite 354, 65 petrolatum 233, beeswax 294, and I. G. Wax OP 1600 to 1900.

I. G. Wax Z, a hydrocarbon wax, has a specific gravity of 0.936 at 25°, 0.930 at 30°, and 0.779 at 112°, which is 10 degrees above its melting point, Z Wax has a higher melting point than any other hydrocarbon wax on the market, and when added in small quantity to the paraffin waxes substantially increases their melting points.

I. G. Wax E has emulsifying and saponifying properties superior to carnauba wax. It contains only 8 to 10 per cent of unsaponifiable matter, which is far less than carnauba. Emulsions with Wax E are remarkably smooth and produce polishes of high luster and permanency.

I. G. Wax S is recommended for the hardening of candles made from paraffin and stearic acid. When treated with alkalies or soaps practically snow white emulsions can be made with I. G. Waxes. Saponified polishes made from it show a pure white color and a fine luster.

I. G. Wax B is recommended as a substitute for beeswax as it is similarly plastic, and can be saponified more readily than beeswax. It is said to have value in cosmetic preparations and increases the flexibility of wax pastes.

I. G. Wax V is a wax with a high degree of solubility in turpentine and its substitutes, and will produce a very high luster. This wax will be referred to under emulsifying waxes. A manufacturer who was exploiting liquid auto polishes combined I. G. Wax OP and candelilla wax, only to find that his product solidified when placed on the market. I. G. Wax OP should be used only for preparations of solid consistency and I. G. Wax V, is recommended for liquid preparations. I. G. Wax V has a very high solubility in turpentine and in coal tar solvents. It is brittle and has a high luster. The combination of I. G. Wax V with other waxes, or V Wax alone, forms a definitely good foundation in liquid polishes for floor, furniture, and motor car use.

I. G. Wax Z has been useful for the waterproofing of paper and cardboard containers used for holding beverages and foods. It also proves to be a useful ingredient in wax varnishes applied to lithographed cardboard; particularly when an unsaponifiable wax of high melting point is required. It is a synthetic paraffin of a much higher melting point than any paraffin on the market, and when added to paraffin provides an excellent "melting point booster," and hardening agent.

I. G. Wax OZK is a neutral, soft wax, which in hardness, structure, and appearance is very similar to the best refined ozocerite. It possesses the property of retarding the evaporation of solvents and reducing the tendency of paraffins to crystallize when added to the latter. It is of value in aqueous wax emulsions. It is recommended for use in production of oil boot polishes, paste or liquid floor polishes.

I. G. Wax N can be emulsified in boiling water without the addition of an alkali. The emulsions are capable of taking up large quantities of organic solvents. It is said to be of value for the preparation of water-containing creams for delicate leather.

I. G. Waxes have found use in the following preparations: floor wax, furniture polish, shoe cream, leather dressing, metal polish, auto polish, carbon paper, crayons, glazed paper, varnish, textile sizes and finishes, fiber finishes, lubricating compounds, waterproofing, shellac bleaching, cosmetics, candles, and rubber compounds. I. G. Wax Z has been useful for the waterproofing of containers used for packaging foods and beverages, the wax being blended with a larger proportion of other waxes for the purpose. It also proves to be a useful ingredient in wax varnishes which are applied to lithographed cardboard, particularly when an unsaponifiable wax of high melting point is required. I. G. Wax OZK, a neutral soft wax, resembles ozocerite in hardness, structure, and appearance. It possesses the property of retarding the evaporation of solvents and reducing the tendency of paraffins to crystallize out when added to the latter. It is of value in aqueous wax emulsions. It is recommended for use in many types of polishes, both paste and liquid.

The price range of the various I. G. Waxes has been 43 to 85 cents per pound depending upon kind and quantity. Despite their relatively high cost as compared with waxes in general, their economic use often works out to considerable advantage.

Diglycol Stearate

A dihydric alcohol, such as glycol or diethylene glycol, can be esterified with a fatty acid by heating the materials, suitably proportioned, under pressure in the presence of a catalyst, *e.g.*, sodium glycerophosphate. After esterification, the water and excess alcohol are distilled off under reduced pressure, the reaction mass is dissolved in benzene or naphtha and filtered, the solvent distilled from the filtrate and the latter run onto chilled rolls, from which the ester is scraped off in waxy flakes or chips. The product is odorless, colorless, tasteless, non-corrosive, nontoxic, and edible. It is soluble in alcohol, benzene and turpentine, and disperses in water in a voluminous manner. A very stable emulsion of mineral oil can be prepared with diglycol stearate. The emulsions are useful in processing cotton, wool, rayon, paper and leather (see emulsifiable wax-like materials, p. 298).

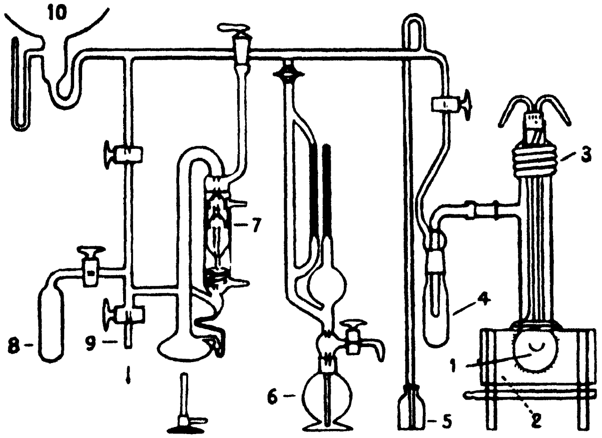
Diglycol stearate is used as a binder for clays as it is consumed without ing a carbonaceous deposit when the clay is fired. However its ipal field lies in making alkali-free emulsions. To disperse the stearate in water it is melted with or without the addition of other wax. Water is heated above the temperature of the melt and added to the latter slowly and with vigorous stirring. Diglycol stearate in water dispersion can be used for the extrusion of aluminum tubing, and in die-forming of paper material into containers. It is valuable in paper work as it leaves no stain on the paper material, and has good lubricating value.

Synthetic Paraffin Wax

Synthetic paraffin wax has been prepared by the Fischer-Tropsch Water-Gas Synthesis in a pilot plant at the Institute of Coal Research, Ruhr, Germany. The water-gas reaction process is employed primarily to make gasoline, but hard paraffin waxes to the extent of 5 to 10 per cent of the total paraffins have been obtained as a by-product, when the high-boiling synthetic paraffin oils have been subjected to chilling. The paraffin obtained has a melting point of 50° (122° F) and consists of the hydrocarbons $C_{17}H_{36}$ to $C_{25}H_{52}$. The catalyst itself becomes saturated with paraffin wax melting at 70° to 80°. An ether-insoluble portion melts at 92°.

Fischer and Koch[7a] obtained a similar product by the catalytic reduction of carbon monoxide at 15 atmospheres of pressure. Koch and Ibing[15] determined that the synthetic hard wax melting at 80° is completely soluble in amyl alcohol, ethyl acetate, petrolic ether, benzene, toluene, xylene, carbon tetrachloride, and certain other solvents. It is partly soluble in propyl alcohol, ether, chloroform, and dichloroethylene, and insoluble in methanol, ethanol, acetone, and methylethyl ketone. They attempted to separate the individual high molecular weight paraffin hydrocarbons on the basis of differential solubility, employing methods of extraction, fractional crystallization and fractional precipitation. They did effect the separation by a procedure involving difference in vapor pressures, that is distillation based upon the work of Krafft on lignite paraffin; the work of Fischer and Glund on waxes present in crude cold tar; and the work of Buchler and Graves, Francis, Myers, and Stegemann, and Ferris, Cowles and Henderson[7] in separating waxes from petroleum. *Molecular distillation* as conducted by Washburn, and improved upon by Carothers, using the micro apparatus for distillations as perfected by Gilchrist and Karlik was resorted to for distilling separated fractions. By means of distillation it was possible to separate the C_{20}, C_{30} and C_{40} hydrocarbons. A portion melting between 102 and 112° was distilled at a pressure below 10 to 25 mu mercury to obtain normal paraffins, C_{50}, C_{60} and C_{70}. At 300° evidence of cracking appears, so that the 110° to 114° melting point residue could not be investigated further. (Figure 19.)

The raw wax for the distillation was obtained by extracting the nickel-manganese-aluminum catalyst, used in the water-gas reaction, for several weeks with benzene.



From: Petroleum Refiner, 22, 9, (1943)

FIGURE 19. Diagram of arrangement for high vacuum distillation, illustrating the principle of the molecular still used by Carothers and his coworkers. *Key:* (1) distillation vessel; (2) aluminum block with spherical depression, electrically heated; (3) circular water condenser; (4) receiver to condense cracked products; (5) barometer; (6) Macleod manometer; (7) mercury pump; (8) receiver cooled with liquid air; (9) connection to oil pump (not shown); (10) large flask used as a pressure equalizer and for vacuum storage.

The extraction was carried out altogether in three successive stages, and the dark colored paraffins were bleached with bleaching-clay at 100° to yield straw-colored odorless products:

Test	M. P.	Aver. Mol. Wt.
1.	70°	570
2.	80°	630
3.	90°	740

They extracted 100 grams of the synthetic wax with 750 cc of ether, and after evaporating to a small volume added alcohol to precipitate snow white crystals which were filtered off on a suction filter, washed free of solvent, and dried. In this way hard paraffins of 88°, 98°, and 106° melting points were obtained. The molecular weights were 700 and 860 for the 88° and 98° melting point waxes respectively. The ether-soluble portion gave waxes of 40° and 60° melting points with molecular weights of 490 and 610 respectively by the Rieche method.

Certain fractional extractions with chloroform and treatment with dichloroethylene led to the separation of hard paraffins of 112 and 116° melting points, having molecular weights of 1750 and 2140 respectively. The chloroform-insoluble residue with molecular weight of over 2000 appeared to be composed of paraffin molecules of approximately 150 carbon atoms. Accordingly it would appear that there could be no normal paraffin of melting point over 118° no matter how large the molecule might become, the iso-paraffins being excluded since they are always of a lower melting point. These high molecular-weight paraffins show a very high dielectric strength.

The following table is that of Koch and Ibing.[15]

Molecular Weight of Several Fractions in Comparison with Those of the Normal Paraffins of Similar Melting Point

Fraction No.	M. P.	Mol. Wt.	*n*-Paraffin	M. P.	Mol. Wt.*
l-d	81.3– 81.8	561	$C_{40}H_{82}$	80.5–81	563
v-f	95.5– 96.4	766	$C_{54}H_{110}$	95	759
vl-f	101.5–102.1	895	$C_{64}H_{130}$	102	899
B-s	91.5– 92.5	687	$C_{50}H_{102}$	91.9–92.3	703

*Calculated molecular weight.

The Fischer-Tropsch synthesis to produce gasoline builds up hydrocarbons of the paraffin series from methane to hydrocarbons of over 150 carbon atoms—quite remarkable since the starting material, carbon monoxide, contains only one atom of carbon. The synthesis forms hydrocarbons never before isolated in petroleum paraffin waxes.

Hydrogenation of Oils

Hydrogenation of liquid fats in the presence of such catalysts as nickel, copper, platinum or palladium into more solid fats, a development first introduced about 1911 has revolutionized the industry. Several processes are used: (1) the agitation process* in which mechanical agitation is used to obtain intimate contact between the liquid fat, the hydrogen and the catalyst; (2) the injection or circulation process in which the liquid fat and catalyst are taken from the lower part of the reaction end and injected as a fine spray into a gas-space at the top; (3) the continuous process in which the liquid fat passes down over a stationary catalyst while a current of hydrogen is forced up through the chamber.

The hydrogenation of oils can be so controlled that the oil is hardened

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*In the Woltman method Brit. Patent, 112,293 (1916)—the material and catalyst are agitated together by rotary perforated arms through which hydrogen is injected. A horizontal steam-jacketed receptacle contains a hollow rotary horizontal shaft through which hydrogen is passed from a pipe and from which it escapes by perforated arms. The duration of contact between the gas and the fat may be regulated, either by providing perforations in one side of the arms only and rotating the arms so that the gas is injected either in or against the direction of rotation, or by dividing the arms by partitions to form longitudinal gas passages which may be separately supplied with gas.

to a definite iodine number or to a definite refractive index number. Since hydrogenated oils are for the most part merely hardened fats only brief mention is made of them here. With hydrogenation the oil loses its oily characteristics and the iodine number decreases with a corresponding increase in the melting point of the material. It is not possible to secure the same tallow from the vegetable oils even by carefully controlling the degree of hydrogenation. There is perhaps a closer approach to tallow with hardened whale oil than with other hardened oils. The Germans use a considerable amount of hardened whale oil for food purposes. The approach of imitation to real tallow is interestingly set forth in these figures:

	Iodine Number	Melting Point
Beef tallow	35.5	43°–44.0°
Hardened linseed oil	35.5	57.0°
Hardened cottonseed oil	35.5	51.0°
Hardened whale oil	35.5	47.5°
Mutton tallow	42.5	45.0°
Hardened linseed oil	42.5	55.0°
Hardened cottonseed oil	42.5	48.2°
Hardened whale oil	42.5	45.4°

Should we reduce the iodine number of cottonseed oil to 20 by hydrogenation, the melting point would be 56°, the product wax-like and easily flaked, suited to meet individual industrial needs, obviously prohibitive as a substitute for beef tallow. Refractive indices of the synthetic fats are directly proportional to the iodine numbers as can be shown by straight line curves. Hence a determination of the refractive index will really give the iodine number for a hydrogenated oil of known purity. A determination of the refractive index is simpler than that of either iodine number or melting point as a control for the degree of hydrogenation.

Hydrogenated Vegetable Waxes. *Hydrogenated cottonseed, soybean,* and *corn oils* are wax-like products. The first mentioned appears on the market in beautiful small flakes,* pure white, odorless, and tasteless, under the name of *Coto Flakes.* These products are all saponifiable. *Hydrogenated cotton seed oil* may be substituted for palm oil when coating the pickled steel sheets in the manufacture of tin plate. Its advantage is that it is far less likely to become rancid in the prolonged heating of the molten bath of tin. *Hydrogenated marine oil* has recently been used for the same purpose at one of the large tin plate mills.

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*The flakes of the wax-like products described are produced by a flaking machine. One type of machine consists of a hollow polished stainless steel cylinder, which can be cooled by circulating cold water, with the intake and output at the ends of the horizontal axis. The molten wax is applied to the periphery of the cylinder from a rectangular melting vessel with a longitudinal gate valve. The solid wax film is removed from the cylinder by a doctor blade. The congealed wax film may then be readily crunched into flakes.

By hydrogenating castor oil a disphanous solid, or wax-like material, can be produced, which is said to be comprised of trihydroxystearin (m. 89.4°) 5 parts, stearodihydroxystearin (m. 74.9°) 10 parts, and distearohydroxystearin (m. 69.5°) 75 parts. The product is referred to as *hydrogenatea castor oil.*

In the past decade it has been found possible to produce very important *higher alcohols* by hydrogenating fats with a suitable catalyst at 200° to 250° and at high pressure—100 to 200 atmospheres. The higher fatty alcohols are valuable as waxes with special properties; also their hydrogen sulfates and hydrogen phosphates yield alkali salts which are finding wider and wider applications as emulsifiers, wetting agents, and detergents. By fractional distillation under reduced pressure the separation of the individual alcohols can be accomplished.

In the Normann[16a] process a mixture of higher alcohols corresponding to the fatty acid radicals of coconut oil is produced by the catalytic hydrogenation of coconut oil with a cobalt-containing catalyst at 285° under about 250 atmospheres of pressure.

Synthetic waxes may be produced in some instances by the hydrogenation of aliphatic alcohol esters, *e.g.*, *cetyl palmitate* (spermaceti), to wax alcohols. Guyer[13] carried out the hydrogenation of these esters as well as that of coconut fat and sperm oil by subjecting the material to a temperature of 250° to 300° and a hydrogen pressure of 150 to 300 atmospheres, using a catalyst of chromium or copper oxides containing 1 per cent of iron. Green[11] carried out the reduction to alcohols by passing a rapid stream of hydrogen at a pressure of 5 to 50 atmospheres through a vigorously agitated mixture of the substance to be treated and a suitable catalyst. The alcohols as they are formed are carried out of the reaction vessel in the stream of hydrogen.

According to an earlier British patent held by E. I. du Pont de Nemours & Co.[6] the reduction from fat or fatty oil to alcohols is effected by treating the substance with an excess of hydrogen at 200° to 400° and 100 to 205 atmospheres in the presence of a mixed cadmium-copper-zinc chromite catalyst. In this way, palm, coconut and castor oils may be converted to wax-like materials.

Opalwax. Opalwax is a brand name given to a synthetic wax of the E. I. du Pont de Nemours & Co., produced by the catalytic hydrogenation of castor oil. *Opalwax* is said to consist principally of 12-hydroxystearin (glyceryl trihydroxystearate).

Opalwax is odorless and tasteless, pearl white in color, of dull to vitreous luster, conchoidal in fracture, and non-toxic. It has a density of 0.980 to 0.990 at 20°. It melts at 86° (186.8° F), and softens at 1° F lower than its melting point. The molten wax has a faint yellow color and is transparent. Opal wax has a durometer hardness of 100 at 25° or below.

Temperature	Density*
24°	0.9896
35	0.9857
90	0.9030
100	0.8960
113	0.8870
130	0.8790

*When cast in chilled molds, a density of 1.000 can be obtained at 20°.

Opalwax has a coefficient of cubical expansion of 0.000784 between its melting point and 110°; 0.000679 between 110° and 120°; and 0.000455 between 120° and 130°.

Solubility of Opalwax in 100 ml Solvent
(*by Ammonia Dept. of du Pont Company*)

Solvent	At 18° to 20° (grams)	At 30° (grams)
Toluene	1.5	1.5
Carbon tetrachloride	1.4	1.5
Carbon bisulfide	1.3	1.9
Xylene	1.2	1.2
Acetone	0.6	1.1
Ether	0.3	1.2
Glacial acetic acid	0.4	1.2

Opalwax is soluble to the extent of less than 1 gram per 100 ml (at 18° to 33°) in the following solvents: isobutanol, Cellosolve, ethanol, methanol, petroleum ether, and methyl Cellosolve. Its solubility in ethanol (95 per cent) is 0.05 gram at 18° to 20°, and 0.40 gram at 33°. Its relative insolubility to other waxes in commercial solvents suggests a variety of applications, where insolubility of a wax is an important factor.

Opalwax when added to other waxes tends to greatly elevate their melting points, partly through greatly increasing sluggishness of melting of the wax mixture.

Opalwax has an acid value of less than 2.0, saponification value of 175 to 185, iodine number of 2.5 to 8.5, and a hydroxyl number of 155 to 165, ash content of less than 0.005 per cent. Its dielectric constant is approximately 12 at 30°; 22 at 60° for 100 cycles.

In making emulsions of Opalwax with water the molten wax (100°) is introduced, with rapid agitation into about two and a half times its own weight of water (85°) in which a small amount of a suitable emulsifying agent (polyvinyl alcohol) has been thoroughly mixed in advance. The emulsion will remain stable when subsequently diluted and yield a continuous film upon drying.

Paraffin (128/130)—Opalwax Mixture

Per Cent of Opalwax	Melting Point °F
0	130
5	158
10	182
20	183
100	187

Ozocerite—Opalwax Mixture

0	162
5	176

Beeswax—Opalwax Mixture

0	152
5	152
10	158

Petrolatum Wax—Opalwax Mixture

0	165
4	181
9	187
20	187

Opalwax is packed and supplied commercially in pearl white flakes. It is used for impregnating and coating papers, fiber board, leather, cork and textiles to make them grease, oil, and waterproof, or as a lubricant for electrical insulation. It is claimed to be of value in the manufacture of candles, rubber-coated fabrics, polishes and finishes, carbon paper, inks, cutting oils, and for waterproofing and air breaking of air plane wings. It is used for polishing cork stoppers.

Waxy Ketones

In general the dialkyl ketones are prepared by the catalytic decarboxylation of the corresponding acids, and are all wax-like solids. This splitting off of the CO_2 group raises the melting point. Suitable catalysts are found in nickel, iron, tungstic sulfide, and alumina. The catalyst powder is spread on the carrier which is silica gel or fuller's earth. The temperature varies to about 370° optimum.

The following dialkyl ketones are recorded:

Name	Formula	Melting Point °C
Laurone	$(C_{11}H_{23})_2CO$	70
Myristone	$(C_{13}H_{27})_2CO$	75
Palmitone	$(C_{15}H_{31})_2CO$	83
Stearone	$(C_{17}H_{35})_2CO$	88
Behenone	$(C_{21}H_{43})_2CO$	92
Cerotone	$(C_{25}H_{51})\ CO$	95
Montanone	$(C_{27}H_{55})_2CO$	97
Myricone	$(C_{29}H_{59})_2CO$	99
Laccerone	$(C_{31}H_{63})_2CO$	104
Geddione	$(C_{33}H_{67})_2CO$	109

Stearone. Grün, Ulbrich, and Krczil[12] heated *stearic acid* for six hours at 300° in the presence of SiO_2, CuO, ZnO, TiO_2, ThO, and obtained 6 to 7 per cent of ketones; CdO gave 13 per cent; Fe oxides, Al_2O_3, Mn on kieselguhr gave 17 to 24 per cent. *Palmitic acid* acts quantitatively with respect to yielding ketone in a period of three hours at 295°; myristic acid acts similarly at 285°. Excellent results are obtainable by Pipping's method in which the higher fatty acids are decomposed by phosphorous anhydride, P_2O_5, with the evolution of CO_2 and water, and the formation of the ketone

$$2R\cdot COOH \longrightarrow R_2CO + CO_2 + H_2O$$

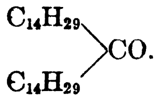
Stearone is produced on a small scale as follows: 9.5 grams of pure stearic acid are heated in a glass vessel at 210° with 5 grams of P_2O_5, adding small portions at a time with constant stirring. At first considerable effervescence takes place owing to the liberation of CO_2. At the end of the operation the brown mass is allowed to cool, and then gradually stirred with water to convert the residual P_2O_5 to phosphoric acid. After adding an excess of sodium hydroxide the mixture is warmed gently, stirred frequently for about 15 minutes, allowed to cool, and diluted with water. The stearone at top of liquid may then be separated by decantation or filtration. The yield is over 27 per cent.

Stearone is also known as *18-pentriacontanone.* It is a pale brown solid as crystallized out from petroleum ether. It boils at 345° at 12 mm pressure. Stearone has many characteristics of stearic acid without the acidity of the latter. It burns with a yellow flame when made into a candle with paraffin. Stearone made from triple pressed stearic acid has a lower melting point than palmitone with which it is associated, namely 78.5°. A mixture of this stearone with paraffin (m. 53.5°) 50 : 50 melts at 70°; stearone 16.6 and paraffin 83.4 parts at 53.5°; stearone 33.3 and paraffin 66.7 parts at 65°. Stearone is compatible with paraffin and forms simple solutions.

Ketones Other Than Stearone. *Myristone,* m. 74 to 75° is found to the extent of 0.23 per cent in dry alfalfa. *Palmitone* is found in the leaves of the sandalwood, *Santalum album,* L., which also contains d-10 hydroxypalmitone, $CH_3(CH_2)_{14}\,CO(CH_2)_5CHOH(CH_2)_8CH_3$. *Montanone* is prepared from montanic acid (m. 86°) by gradually heating the acid at 200° for a long period of time, which causes the CO_2 groups to split off. By heating red oil (oleic acid) in iron kettles used in the preparation of the acid, *oleone,* $C_{35}H_{66}O$, m. 59.5°, results. Similarly *elaidone,* $C_{35}H_{66}O$, m. 70°, and *brassidone,* $C_{43}H_{82}O$, m. 80°, result.[5]

Uses for Ketones. The dialkyl ketones may be melted with hydrogenated oils to produce imitations of the hard natural waxes. For example, *behenone* when melted with Opalwax, which is a hydrogenated castor oil, produces a substitute for carnauba wax in polishes.

The dialkyl ketones could undoubtedly be put to many varied uses were they made available to the market at an attractive price. The hydroxy ketones make suitable substitutes for other waxes in polishes, and in foundations for carbon papers. Tressler and Schade[24] converted an unsaturated ketone (*i.e.*, oleone) by treatment with concentrated sulfuric acid into ethereal sulfate which was then hydrolyzed to form the hydroxy ketone. This hydroxy ketone is reported as a substitute or replacement wax for Chinese insect wax in floor polishes.

Dialkyl ketones with an odd number of carbons are occasionally found in nature; *e.g.*, the cytoplasm of the cabbage leaf, *Brassica oleracea*, L., contains ditetradecylketone,  $\begin{matrix} C_{14}H_{29} \\ C_{14}H_{29} \end{matrix}\!\!>CO$. .Ordinarily the dialkyl ketones are symmetrical, but are not necessarily so.

The aryl-alkyl ketones are unsymmetrical ketones in which the two hydrocarbon groups involved are cyclic and straight chain respectively. For example, *methylheptadecyl ketone*, $CH_3 \cdot CO \cdot C_{11}H_{23}$. Such ketones are prepared by the Friedel-Crafts condensation of acids, anhydrides, or acid chlorides with aromatics such as benzene, anthracene, or xylene. According to Ralston[19] they show high polarity at the carbonyl group—(CO) group—and are miscible with a great number of substances.

Wax Secondary Alcohols. The preparation of wax secondary alcohols has been conducted by Grün, Ulbrich, and Krczil[12] by heating the ketone and ethyl alcohol in the molecular proportion of about 1 : 2 with the calculated amount of sodium hydroxide in water at a temperature of 300° for 6 to 8 hours. The following compounds were made:

pentatriacontan – 2 – ol $(C_{17}H_{35})_2CHOH$
hentriacontan – 2 – ol $(C_{15}H_{31})_2CHOH$
heptacontan – 2 – ol $(C_{13}H_{27})_2CHOH$
tricosan – 2 – ol $(C_{11}H_{23})_2CHOH$

The transforming of a wax secondary alcohol into the corresponding olefin by way of the alkyl chloride presented no difficulties. One mole of the secondary alcohol was heated with two moles of $SOCl_2$ for two hours; the excess of the latter removed under a vacuum and the reaction product crystallized from ethyl acetate, ether, and then alcohol to a constant melting point.

Wax Esters. Wax esters were prepared by allowing the chloride of the acid to react in slight excess with alcohol on the water bath while passing a stream of CO_2 through the reactants. After the free HCl ceased to be evolved the free acid was neutralized with alcoholic potassium hydrate and the ester and fatty acids salt separated by petroleum ether and alcohol 1 : 1. To separate the unesterified wax alcohol the reaction product was extracted with hot ethanol in which the esters are insoluble. They were then crystallized from various solvents to a constant melting point. The yield was 90 to 95 per cent.

Wax esters may be produced by treating various oils with aluminum oxide or zinc oxide added to the copper-chromium-oxygen catalyzer used for hydrogenation. The wax ester produced from soybean oil, according to Sinozaki and Adati[22] is more easily soluble in alcohol and somewhat less soluble in turpentine than beeswax. The melting point and viscosity in turpentine solution of the ester is like that of beeswax, making it possible to use such a wax as a replacement wax for some purposes.

Alkyl Cyclic Ketones. Ralston and Christensen (Armour & Co.)[19], found that furyl alkyl ketone reaction products of stearyl, myristyl, lauryl, and caproyl chlorides with furan were for the most part waxy solids suitable for use in electric insulation, in waxing and polishing compositions and as an addition to lubricating oils. *Furyl heptadecyl ketone* melts at 52.5 to 54.0°, *methyl furyal heptadecyl ketone* melts at 68 to 69°, *dibenzofuryl heptadecyl ketone* melts at 83 to 84°, and the corresponding *hendecyl* compound at 74 to 75°. They also found mixed phenoxyphenyl alkyl ketones to be of similar value. The general formula is RCOR′, where R′ is a phenoxy and R an alkyl radical. The aralkyl ketones are waxy solids and can be crystallized from benzene, alcohol to give pure ketones. *Phenoxy phenyl heptadecyl ketone* melts at 68°. Diphenylyl alkyl ketones, where R is the diphenyl radical, have similar wax properties. *Diphenyl heptadecyl ketone* melts at 108–109°, the *tridecyl* compound at 102–103°, and the *hendecyl ketone* at 97–98°. These ketones of the Ralston and Christensen[19] patents can be made by the Friedel-Crafts reaction or by the Grignard synthesis.

Stearamide

Stearamide and other amides of the higher fatty acids are neutral chemicals of a high-melting, wax-like nature. They appear to have been first prepared commercially by the Chemische Werke Hansa,[3] Hemelingen, Germany in 1906, by the simple well known reaction

$$R\cdot CO\cdot OH + NH_3 = R\cdot CO\cdot NH_2 + H_2O$$

The method consisted of melting down the stearic acid in a closed vessel, and while heating the melt passing gaseous ammonia through the mass under a carefully regulated pressure. Kösters and Otteman of Bremen[15a] improved upon the process by a system of continuous circulation of the ammonia gas, withdrawing the water and ammonia during the reaction and returning the ammonia in a dried form to the autoclave. In the United States this class of amides have been given the trade name of "Armids" by Armour and Company. The Armids as marketed vary in physical structure from a substance which can be flaked, to a soft paste. They are not soluble in water. "Armid HT" melts at 98°, is a wax-like solid with a carbon chain length of 16–18 saturated. "Armid C" melts at 90°, and has a carbon chain length of 12–18 saturated. The paste-like Armids are associated with unsaturated carbon chains.

The Armids act as mutual solvents for waxes and plastics. They are used to the extent of 2 to 5 per cent as anti-tack or anti-block agents in plasticized synthetic resin formulations, and hence are of value in hot melt compounds used for coating sheet material. Fluid coatings and plastics can be made with the Armids by employing straight petroleum solvents, or with the addition of butyl alcohol. In making composition for dental use a preferred light color may be maintained by melting the composition under a blanket of inert gas, such as nitrogen or carbon dioxide. An important use of *Armid T* is as an agent for blending ethyl cellulose with wax, and a little diphenylamine is said to prevent heat discoloration of the ethyl cellulose. Other uses for long chain aliphatic amides are as a dye solvent in carbon paper manufacture, for candle dipping, for polishes, and for textile softening and sizing emulsions. They must not be heated beyond 170°, nor boiled with acid or alkali, since they undergo decomposition.

COMMERCIAL COMPOUNDED WAXES

Obviously it is possible to produce innumerable mixtures or blends of the natural waxes, far more than could be described. Hence, only the compounded waxes ordinarily obtainable in commerce will be here considered. At the same time compounds that are not waxes but prepared with wax as the principle ingredient will be discussed. These blended waxes and compounds can be grouped as follows:

Blended waxes

(1) Blended natural waxes, inclusive of the various petroleum waxes.
(2) Natural waxes compounded with synthetic waxes.

Compounds containing waxes

(3) Waxes combined with resins.
(4) Waxes combined with natural or with synthetic rubbers.
(5) Waxes compounded with resins and rubbers.
(6) Waxes compounded with cellulose ethers.

Of the six groups (1) is most important commercially, both in volume and broadness of use. Over 90 per cent of this group comprise the artificial ceresin waxes, usually designated simply as "ceresin waxes."

Although occasionally the commercial ceresin waxes are referred to as "imitation ceresins," which they are for the most part, the word "imitation" is seldom used in connection with them. In the industrial arts there has always been a demand for more or less plastic waxes of relatively high melting point, *viz.*, 63° to 73°, which are devoid of any pronounced macrocrystalline characteristics, and which are unsaponifiable, or nearly so. To meet this demand the wax converters have offered these so-called "ceresin waxes" in qualities ranging from the cheapest to the best and most expensive.

The base of the ceresin wax of commerce is *paraffin, scale* or *refined,* or both; to which is added *candelilla, carnauba,* or *montan wax* as a hardening agent and as a means of raising the melting point; and *beeswax, ozocerite, microcrystalline petroleum wax,* or other suitable wax as the "decrystallizing agent." Ceresin waxes are offered in many colors; *i.e.*, white, yellow, orange, brown, and black.

The name "genuine imported ceresin" does not necessarily indicate that this ceresin is the same as "ceresine," a name originally given to the mineral wax-ozocerite. The wax offered as "genuine" is in reality a composite of the refined wax distillates from brown coal admixed with the mined and bleached ozocerite. It is a very good quality wax with a high melting point, and will be described later. It is "genuine" in that it is free from carnauba wax, montan wax, or other additive material.

Synthetic waxes are occasionally blended with natural waxes, but usually in only small amounts. Most often the synthetic wax is used to elevate the melting point of the base wax, or as a hardening agent. For example *I. G. Wax Z* may be added to a petroleum wax, or *Opalwax* added to a *ceresin wax,* in the proportion of 1 or 2 per cent. Synthetic waxes will not always mix with paraffins, or if they do mix, settle out on cooling.

Waxes can be compounded with resins, although not always freely so. Considerable is known about the compounding of the waxes with the natural gums, such as dammar, the copals, and colophony. Less is known about the compounding of waxes with synthetic resins. Waxes will mix with coumarone-indene, Aroclor, Nypene, and some other resins. Some of the synthetic resins are not compatible with waxes. Normal butyl methacrylate resin will not mix with paraffin wax, but will combine readily with beeswax.

Wax can be compounded with rubber to a limited extent. There are various means of incorporating the wax in the rubber, and these methods appear to have been covered by several letters patents. Wax is more readily combined with a rubber derivative obtained by subjecting the rubber to a so-called "cyclizing process" (see Pliowax, p. 292). Wax is somewhat difficult to combine with Buna S synthetic rubber, but it can be "milled in" using warm rolls. Wax can more readily be incorporated in Butyl rubber.

The addition of resins and rubber to wax so changes the physical characteristics of the resultant compound that it is no longer wax-like. Some of these wax-rubber-resin compounds make good adhesives.

The Compounding of Waxes

When a small amount of one kind of wax of a much higher melting point (No. 1) is melted with a much larger amount of a relatively low melting point (No. 2), the resultant congealed wax product will melt at a temperature which will indicate a state of (a) solid solution with No. 1 the solute, and No. 2 the solvent, *i.e.*, a double phase system; (b) a simple wax mixture (single phase); (c) a true compound; or (d) an incompatible mixture.

In system (a), No. 1 greatly elevates the melting point of No. 2, as sugar elevates the boiling point of water. Under certain conditions No. 2 may liquate out, just as water will separate from a sugar solution.

In system (b) when the melting points are plotted against the percentage composition the curve is a straight line or nearly so; *e.g.*, mixtures of the paraffins; or waxes of similar molecular weight and type, such as the vegetable waxes.

In system (c) eutectic compounds with melting points lower than No. 1 are formed, and the plotted curves flex sharply downward; *e.g.*, melts made with pure palmitic and stearic acids.

In system (d) the No. 1 constituent tends to gravitate out even though it may be miscible in the melt. That very small portion which is soluble acts like (a), but a larger portion is simply dispersed. *E.g.*, mixtures of Opalwax with paraffin.

There are also instances where more than one system is involved as can readily be seen by a study of the areas involved in the plotted curves.

Compounded or blended waxes when prepared on a commercial scale are made by melting the different waxes in a steam jacketed or electrical heated kettle made of aluminum or stainless steel. If electrically heated, the heating units are extended over the lower two-thirds of the vessel so as to avoid overheating at the top. The units must be properly packed with insulating material and wrapped on the outside so as to focus the heat on the interior of the kettle through the walls of the vessel. The lower melting point wax is melted first, and the higher melting waxes are then added. The blending of the waxes is effected by stirring them with a wooden paddle, although a double blade mechanical stirrer is to be preferred. In melting waxes it is best to carry out the process at a temperature of not over 28° (50° F) above the melting point of the finished wax compound, in order to avoid any alteration of the composition of the components. A melting kettle usually has a gate valve at the bottom or to one side of the vessel. After opening the gate the melted wax should be strained through a fine metal screen, or through layers of cheese cloth, into an enamel-lined or other suitable pail with a broad pouring lip, from which the wax is poured into pans and permitted to solidify. These pans are either oblong or round and tapered. Pans made of aluminum are the most satisfactory. The wax is allowed to cool at room temperature until it becomes perfectly solid, but the removal of the wax is greatly facilitated by immersing the pan with the wax in ice water for a few minutes before tapping the bottom of the inverted pan to remove the cake of wax.

In compounding waxes difficulty is sometimes experienced with their proper blending. By mixing the wax ingredients in an autoclave with an agitator a superior blended product can be obtained with the aid of pressure. According to Dickinson[4a] the resultant wax by virtue of its improved hardness, plasticity, and melting.point, is better for rendering paper transparent.

Imitation Ceresin Waxes

Under the name "ceresin," or a closely allied name, there is offered on the market a great variety of waxes, from white to dark yellow in color, in melting points ranging from 135° to 165° F or higher. These imitation ceresins often bear brand names like "Four Star," "Snow White," "Marble White," "Special Seal," etc. Generally speaking these commercial waxes have a melting point above 60° (140° F), have little or no saponifiable matter, are masticable, and free from any objectionable taste or odor. These imitation ceresins have a specific gravity of 0.910 to 0.920 at 25°, and like *ozocerite ceresin* of genuine origin, are soluble in benzine, chloroform, benzene, hot oils, and slightly soluble in ethanol; they are also equally compatible with other waxes.

Imitation ceresins have been made in the past by blending ⅔ *paraffin* and ⅓ *ozocerite*, have served nearly as well as ozocerite itself for many purposes, and are much cheaper. However, the melting point of such a mixture is appreciably lower than that of ozocerite, By adding a very small amount of carnauba wax to the melt, it is possible to produce a ceresin having exactly the same melting point as the genuine ceresin. To lower costs the quantity of paraffin can be increased with an increase in the admixture of *carnauba wax*, thus reducing the amount of the costly ozocerite component; *e.g.*, paraffin (128 to 130° F) 82, refined ozocerite 15, and carnauba wax 3 parts.

When it is desirable to produce a flexible artificial ceresin with a high melting point, a high melting hydrocarbon wax such as I. G. Wax Z may be added to a crude scale wax, and also sufficient carnauba wax to bring up the hardness and toughness. I. G. Wax Z melts at 218° F, softens at 176° F, and has a hardness of 100. When added to scale wax (m. 125° F) the I. G. Wax will break the macrocrystalline structure of the scale wax, and elevate its melting point. For example, starting out with 95 parts of scale wax the addition of I. G. Wax Z 2 parts, and carnauba wax 3 parts will raise the melting point from 125 to 148° F, the softening point from 98 to 105° F, and the durometer hardness from 30 to 50 at 82° F, and from 67 to 77 at 34° F. Therefore the addition of these two waxes to scale wax to the extent of only 5 per cent increases the melting point 23° F, the softening point 7° F, and the hardness as much as 20 points at 82° F.

A *black ceresin* has appeared on the market as a "replacement wax" for *black ozocerite*. The wax has a specific gravity of 0.925 at 25°, a melting point of 85° (185° F), a softening point of 82° (179.6° F), a congealing point of 84° (183.2° F), ash 0.16 per cent, penetration at 25° of 7 to 8 per 100 grams in 5 seconds. It is acid and alkali resisting, non-saponifiable, very flexible, and of high dielectric strength. The wax closely resembles a black microcrystalline petroleum wax.

The American market price on imitation ceresins will normally range from 7 to 27 cents per pound according to grade, the average price being 14 cents for a wax of good quality. The great scarcity of genuine ozocerite ceresin in America during World War II forced the price from 30 to more than 60 cents per pound, and resulted in the use of selected grades of microcrystalline petroleum waxes as a replacement for ozocerite in the compounding of imitation ceresins.

The white ceresin waxes are found extensively in waxed paper material, lubricants, wax figures, waxed cloth, bottle cap liners, pencils and crayons. The yellow ceresins are employed in the radio, rubber, electrotype, sound record, plastic and abrasive industries. They are also used for the insulation of electric cables, the molding of electrical equipment, the coating of barrels and cans, and the preparation of waterproofing compounds, inks, carbon papers, and shoe polishes.

Italian ceresin has a melting point of 72° (161.6° F), is snow white in color, odorless, tasteless, tough and flexible, and free from the "tack" of Galician ozocerite. It has been sold in New York under the name of "Genuine Imported Pure White Ceresin." It is well suited to waxing papers used for dairy products.

Paraffin-Carnauba Wax Blends

Carnauba wax when fused in *paraffin wax* elevates the melting point of the latter to a pronounced degree, more so than the addition of any other natural wax. The addition of but 10 per cent of carnauba wax will bring the hardness of the resultant mixture to within a few points of carnauba wax itself. The table shown below is based on a mixture of paraffin wax (m. 130° F) and carnauba wax (gordurosa).

Per Cent Carnauba	Dry Melting Point (°F)	Wet Softening Point (°F)	Spread (°F)	Durometer Hardness	
				(at 52°F)	(at 73°F).
0	130	110	20	77.0	60.0
1.2	144	113	21	—	—
2.5	170	115	55	—	—
5.0	175	119	56	88.0	67.0
7.5	177	126	51	—	—
10.0	178	129	48	95.0	74.0
15.0	—	—	—	96.5	80.0
20.0	178.5	143	35.5	97.0	85.0
25.0	—	—	—	97.0	87.0
30.0	178.5	151	27.5	—	—
40.0	179	153	26	—	—
50.0	179	160	19	97.0	88.0
60.0	179	166	13	—	—
70.0	179	169	10	—	—
75.0	—	—	—	97.5	89.0
80.0	179	173	6	—	—
90.0	182	177	5	—	—
100.0	186	182	2	98.0	90.0

The incorporation of 3 to 5 per cent of carnauba in mixtures of waxes is quite a common practice. If 20 per cent of carnauba is added to paraffin wax, the resultant product is quite resistant to water to at least pasteurizing temperature. The addition of higher amounts of carnauba (20 to 50 per cent) is of no practical value, as the resultant waxes shrink and crack.

High Tensile Strength Wax

It has been already shown that the presence of oil in a wax decreases its tensile strength. Paraffins of 130 and 136° F melting point when oil-free have a tensile strength of 390 to 395 pounds per square inch. The addition of about 0.5 per cent of oil will bring the tensile strength down to about 70 pounds. However, the addition of petrolatum wax (10 per cent oil content) will greatly increase the tensile strength of the oil-containing paraffin, as shown by Adams and MacLaren.[1a] The following tensile strengths were obtained:

Wax Composition		Melting Point (°F)	Tensile Strength (lbs/sq in)
95% Paraffin 5% Pet. Wax	133° - 0.5% oil 167° - 10% oil	135.0	156.0
95% Paraffin 5% Pet. Wax	138° - 0.5% oil 147° - 10% oil	138.5	210.0
99% Paraffin 1% Pet. Wax	136° - 1% oil 158° - 10% oil	136.0	280.0
95% Paraffin 5% Pet. Wax	136° - 1% oil 158° - 10% oil	136.5	292.0
90% Paraffin 10% Pet. Wax	136° - 1% oil 158° - 10% oil	137.5	256.0

Replacement Waxes

The word "replacement" as applied to waxes is a term which has found its way into the literature on waxes and is perhaps deserving of mention. A "replacement wax" is a substitute for a well known wax when the latter is no longer obtainable, or obtainable only at a prohibitive price. The shortage of natural waxes and other commodities in World War II created the need for "replacements," or so-called "ersatz" material.

Glickman[10] attempts to distinguish between "substitutes" and "replacements." He defines substitutes as those compounds which may be directly utilized in lieu of the original compound (wax) without requiring any modification of the formulation or procedure in order to obtain an equivalent finished commercial product. "Replacements" are defined as materials which may be used in place of the original wax, but which require some modification in formulation and/or processing to achieve results equal to those obtained with the natural product.

"Compounded waxes" on the other hand are blends of the natural waxes, or mixtures of the natural waxes with resins, etc.

"Replacement waxes" have appeared on the market which imitate the properties of beeswax, japan wax, carnauba wax, and white montan wax. These replacements are offered under various trade names. The "Beacon" line of waxes is of this order.

An imitation of carnauba wax made by Corkery[3a] was prepared by combining stearin or palmitin with a coumarone indene resin melting above 100° and soluble in mineral spirits. The proportion of glyceryl ester to resin was 2 : 3 or 3 : 2. A similar product had a specific gravity of 0.995 at 15°/15°, melting point 76° to 77°, saponification value 88.6, acid value 14.8, ester value 73.8, and iodine number (Hanus) 13.8. Both acid and iodine numbers are higher than those found in carnauba wax, and the color much darker, or a dark brown. A "replacement wax" for carnauba has also been made by melting together *behenone*, a waxy ketone, and hardened castor oil in the proportion of 20 to 80 to produce a wax-like product of high melting point and hardness. In general, glycol or glyceryl esters of 12-hydroxy stearic acid may be reacted with keto, or hydroxy compounds of the fatty acids, having melting points below 70°. Another "replacement" for carnauba wax has been made by cooking or saponifying fatty oils with calcium hydrate, and mixing the reaction product with candelilla wax. The replacement is said to be of value in wood, metal or leather polishes.

Resin-Wax Mixtures

Wax can be effectively compounded with an esterfied polymerized rosin by simply melting the two together, and then applying the combination in the molten state to the surface which it is desired to waterproof. Fibers, fabric, paper, and other surfaces may be so treated. Ester gum made from plain rosin may be mixed with wax, but does not form permanently stabilized compounds; that is, there is a tendency for the constituents to separate on remelting. Esterified polymerized rosin may be prepared from polymerized rosin and glycerine, or any of the glycols; *e.g.*, by heating together molten polymerized rosin 90.5 parts and glycerin 9.5, maintaining the temperature at 280° for a suitable time. The wax used is ordinarily paraffin, but carnauba, candelilla, beeswax, montan, ozocerite, stearic acid, and cetyl alcohol may be used in its place. The polymerized rosin is rosin which has been polymerized in solution by agents such as sulfuric acid, boron trifluoride, anhydrous aluminum, tin, zinc, or titanium chlorides, or by ultraviolet light. The coated papers may be used for food wrapping as they are non-toxic.

A rosin-microcrystalline wax composition for filling up the meshes of reticular sheets, and which according to Warp,[25] can be readily made by melting together 2 parts of natural water white rosin (m. 170° F), with 1 part of *microcrystalline paraffin wax* (m. 160° F). The homogenous mass is applied to a wire screen by dipping the sheet into a molten bath of the composition preferably maintained at a temperature of 250° F or higher. The excess composition can be doctored or scraped off the dipped sheet. A layer of the desired thickness is thus obtained, preferably just sufficient to embed the wires in the layer. The coated screen is cooled by water, or otherwise. The product is weatherproof, flexible, and semi-transparent. The composition film fills up the meshes of the screen and adheres to the screen wires with great tenacity. Anilin dyes premelted with stearic acid make suitable coloring agents.

Various mixtures of natural resins with waxes and wax-like substances were studied by Allan.[1b] The resins used were commercial grades of dammar, Manila, Congo, kauri, and elemi. The waxes comprised *beeswax, carnauba wax, montan wax, japan wax, ozocerite,* and *paraffin.* In general, the resins are completely miscible in the waxes studied, although certain of the fossil resins, and some Manila resins, are not at all compatible with paraffin. The mixtures find application in coating, sizing, and impregnating paper, in transfer inks, in polishes, and candles, in molding and water-proofing compositions, and as linings for metal food and beverage containers. The mixtures can be emulsified with triethanolamine, or other alkaline compounds that will form soaps.

Rubber-Wax Compounds

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A new art has developed in dispersing rubber in wax resulting in the production of flexible wax films of considerable tensile strength and in which certain combinations can be made self-sealing by the application of a hot iron. For example rubber latex is incorporated in paraffin wax to procure tough stretchable film materials that can be sheeted. Crepe rubber is dispersed in wax, in relatively large amounts such as 25 per cent, using microcrystalline paraffin waxes of high melting point. A wax such as *Petrosene A* can be milled in crepe rubber to the extent of 52 per cent but not much beyond this point. In milling, after the crepe rubber has lost its nerve on the mill, the wax is immediately introduced in small portions at a time and in any quantity up to the optimum. Where Buna S synthetic rubber is used it is desirable to added a few per cent of resin in order to secure a better bond with the paraffin.

The concentrated wax-rubber mixtures described above then serve as starting points for the incorporation of small amounts of rubber in various wax coatings, to secure impermeability to liquids, and, in general, to reduce the porosity and improve the tensile strength of the resultant plastic wax films.

Containers for soap made of paper or wood pulp are made resistant to alkalies by impregnating them with a mixture containing *paraffin* and rubber latex. On the dry basis the rubber may be as high as 7 to 8 per cent. Instead of paraffin other waxes may be used in part or whole in the blending with rubber. Kraft can be waterproofed by means of rubber-wax blends. In some instances the rubber-wax compound also has some plastic resin incorporated, making it suitable for protectively coating cardboard containers that take the place of the all-metal or tin canisters.

The use of rubber-wax compound in wrapping cheese is extensive. Usually the rubber-wax is applied in a thin film, of tissue paper thickness, to cellophane and the waxed side of the wrap adheres to the cheese. The use of wax-rubber as a coating medium on other films for heat sealing purposes is described later on.

Pliowax. Pliowax is a combination of *Pliolite resin* and paraffin, and is prepared by incorporating the unmilled resin powder into paraffin wax. Pliolite resin is a synthetic derivative of rubber which is formed by a cyclizing process. "Pliolite" results from a reaction between crepe rubber and a tin salt, such as stannic chloride or chlorostannic acid. It has the same chemical composition as the natural rubber from which it is derived, but it does differ in its structural formula; the aggregation of the isoprene (C_5H_8) molecules are cyclic in the case of Pliolite.

The process of preparation of Pliolite (Marbon Corp., Delaware)[9] involves dissolving the rubber with a suitable solvent to form a heavy, viscous, non-drying cement. The rubber cement is then placed in a jacketed reactor equipped with a reflux condenser and heated for a period of time with a reactant and catalyst; *e.g.*, hydrochloric acid and anhydrous stannic chloride. During this heating period an enormous reduction in the viscosity of the solution is expericed and a physical change is effected from the usual rubber into the resinous state. The reaction is stopped by water and the resin is recovered from the solvent as a finely divided powder which is vacuum dried. The powder is milled to yield solutions which will produce heat-sealing film materials, but if admixtures of Pliolite and wax are desired, where wax is to predominate, it has been found that the Pliolite resin powder very readily dissolves in most of the common waxes, by a process of heating the wax and then adding the unmilled resin. *Pliolite* is not to be confused with *Pliofilm* an exclusive product of the Goodyear Tire & Rubber Company, which is a plasticized rubber hydrochloride. *Petrolatum, beeswax, ceresin,* or hydrogenated oils may be used instead of paraffin, to blend with the Pliolite.

Pliowax is gray-brown in color, but is nearly white in thin film form. It contains 20 to 30 per cent of the Pliolite resin. The melting point is somewhat higher than that of the paraffin from which it is prepared. The addition of unmilled Pliolite resin to a paraffin m. 135° F is said to increase its melting point 3 degrees for every 5 per cent of Pliolite added. However, it is not certain whether such an increase in the melting point would persist in the seasoning of the Pliowax. Pliowax containing 25 per cent of milled Pliolite (Goodyear Tire & Rubber Co., Inc.) had a melting point of 56° (132.8° F), and a softening point of 45° (113.0° F), a hardness of 95 at 24° (76° F) and a specific gravity of 0.9372 at 5°/15°. The wax showed considerable plasticity and elongation at temperatures between 45° and 49°. Another sample which had 29.1 per cent of rubber resins upon analysis had a hardness of 70 at 24°, and 90 at 0°; and melted at 57° (134.6° F).

The viscosity of Pliowax melts is higher than that of paraffin, and the molten wax adheres to smooth surfaces more tenaciously than does paraffin. There is also less tendency of Pliowax to penetrate the material that is coated, and the waxed surface is tougher and is less apt to crystallize.

Pliowax may be diluted with further quantities of wax simply by melting the materials together. This is best accomplished at a temperature not over 180 or 190° to prevent any deterioration. From the x-ray diffraction patterns Thies[23] found that Pliolite, when present in 9 to 10 per cent, gives a true solution with paraffin at room temperature. A film of Pliolite and paraffin (90 : 10) is optically clear even though the x-ray pattern does not show the crystalline paraffin ring to be present. The solubility of the wax in Pliolite increases with the temperature up to the melting point of the wax when both become mutually soluble in all proportions. The Pliowax films are tougher and more lustrous than the wax alone.

Pliowax is applied to paper by a hot dip process similar to the conventional process of paraffining. Even with low concentrations of Pliolite in the Pliowax, the adherence of the coating is appreciably increased and the waterproofness of the waxed paper is greatly enhanced. According to the Goodyear company several million paper milk and fruit juice containers have been processed by this type of product. Other uses are in the fabrication of frozen food containers and the coating of paper for bread wrap. Pliowax may be used as a cheese coating. Greaseproof coatings may be applied to paper or cardboard not only for waterproofing, but for heat sealing, and these containers used for fats and oils.

Pliolite-Wax. Pliolite-wax is the designation given to a composition which differs somewhat from *Pliowax* above described, in the following manner: Instead of fusing *unmilled Pliolite* with wax by heating them together, the wax is incorporated in *milled* Pliolite on mixing-rolls, or in a Banbury mixer. A particular advantage of this process is that it broadens the scope of application, since small amounts of other material may be incorporated in the Pliolite-wax during the milling, when and as desired.

In milling, the Pliolite powder, a finely divided white material, is massed by passing through a tight mill once, and is then banded slowly on the mill until the thermoplastic mass forms a bank. To make rubber-Pliolite mixtures, it is necessary to put the Pliolite on first, and add the rubber slowly in the beginning until approximately 10 to 15 per cent of the rubber is in the batch; then the relative speed of the rubber addition can be reached. The wax is incorporated in the desired quantity and the batch completed.

Pliolite-wax is suited to laminating paper boards, since it will form a water-insoluble bond between the plies, and give flexibility to the resultant plyboard. Added to paraffin, Pliolite-wax prevents crystallization. Its use has been suggested for the making of mounts, wherein its tough viscous properties make it less liable to flow in warm weather than paraffin.

One of the special advantages of Pliolite is that large amounts of wax may be incorporated in it, and the sheets so coated are non-blocking, and can be made heat-sealing where they are ironed or otherwise heat treated. These characteristics are of value in the design of waterproof paper packages to be used in the packaging of dehydrated foods, etc.

Pliolite-wax, or Pliolite plus paraffin, dissolved in a suitable solvent can be applied to the surface of freshly prepared concrete, making it substantially impermeable to water and retarding the evaporation of water from the concrete, thus enabling it to cure properly. This is the method of Scripture.[21]. Scripture gives several compositions, *e.g.* xylene 1 gallon, rubber resin (Pliolite) $\frac{2}{3}$ pounds, and paraffin 1 ounce. On drying this leaves a film containing 91.5 per cent rubber resin, and 8.5 per cent paraffin. A suitable coating for a concrete floor may be prepared from xylene 1 gallon, rubber resin (Pliolite) 1 pound, Halowax 1½ pounds, pigment 10 ounces. The application may be made by brushing or spraying.

Sealz Waxes. Sealz waxes of Dispersion Process Inc. are waxes in which rubber has been incorporated in hydrocarbon waxes of high melting point, such as paraffin m. 140 to 142° F, or on the other hand petrolatum wax m. 160° F. The proportion of rubber to wax is 25 : 75. A Sealz wax made with refined paraffin showed a melting point of 176° F, one made with a petrolatum wax a melting point of 188° F. The rubber used is believed to be unvulcanized. The hardness of a Sealz wax of the lower melting description was found to be 92 at 36° F and 75 at 76° F; that of the higher melting point was softer. The hardness of the latter was 70 at 36° F, and 45 at 76° F, probably because of the softness of the petrolatum wax used in its composition.

The Sealz waxes are used essentially as rubber-wax concentrates and in small amounts can be advantageously blended with other waxes to increase the melting point of the latter. In the concentrate, the presence of each 5 per cent of rubber in the wax increases the melting point by 5 degrees Fahrenheit.

Wax-Rubber Coating on Plastic Films. Wax-rubber is being used to-day as a coating for flexible waterproof film materials in food packaging. By applying to a rubber hydrochloride film a wax-rubber coating, the film material is improved by making it odorless and tasteless in relation to the food it contacts and in other qualities. The coating composition is prepared by melting paraffin wax and adding 6 to 30 per cent by weight of rubber, while the temperature of the melt is held at 180 to 200° F. A Werner-Pfleiderer mixer is used to incorporate the thin pale crepe sheets. According to the process of Abrams *et al*[1] the wax-rubber composition while hot is applied to the Pliofilm. A translucent sheet results which may be stretched 400 per cent of its original length without damaging the base sheet or coating. A further advantage of the wax-rubber coating is that its fusion point is below that of the base, and it is thus possible to heat seal Pliofilm in packaging without distorting the chlorinated rubber film.

Cellulose Ether Wax

An alkyl ether of cellulose, as typified by ethyl cellulose, may be incorporated or used with waxes to obtain wax compounds of considerable value in the arts. Ethyl cellulose is not miscible directly with paraffin waxes, but it can be easily incorporated in waxes that have saponifiable constituents in their natural chemical composition; for example, beeswax. When beeswax is heated considerably above its melting temperature, with efficient mechanical stirring, up to about 25 per cent of the cellulose can be incorporated. Lower amounts of ethyl cellulose such as 5 or 10 per cent are more readily incorporated, that is, dispersed. The *cellulose ether waxes* are non-crystallizable, smooth in texture, and high in melting point, but their high viscosity limits their broad industrial application. Coating compositions or resins, plasticizers, and waxes, may have the cellulose ether added to them to improve their homogeneity, smoothness, tensile strength, and chemical resistance. When pigmented with colors such compositions are of value for crayons and pastels.

In the Kropscott[15b] process the wax is melted in hot water (90 to 95°) and dispersed by vigorous agitation. An emulsion of the cellulose ether is then added to the agitated molten wax dispersion. The solvent contained in the emulsion can be driven off with the aid of steam. The cellulose ether precipitates and immediately absorbs the wax to form uniform granules. After cooling the granules are removed and dried in an oven or in a shelf drier. Instead of using the process described, the water-wet cellulose ether can be suspended in hot water and finely ground wax slowly added during agitation. Alcohol is a suitable medium for wetting the cellulose ether, for example by heating dry ethyl cellulose in a 20 per cent solution of ethanol in water. The wax content in the final product may be regulated from 2 to 60 per cent to obtain a free-flowing granular article.

Montan wax, paraffin, candelilla wax, hydrogenated cotton oil wax, carnauba wax, petroleum ceresin, esparto grass wax, stearamide, or mixtures of two or more of these substances may be used as the wax foundation for the cellulose ether waxes. Hydrogenated castor oil wax is particularly useful for the purpose. The cellulose ethers may be methyl, propyl, butyl, methyl ethyl, ethyl propyl cellulose, and the like.

Kropscott has given the properties of granular ethyl cellulose compositions comprising wax. They are rated on basis of ethoxy content.

Ethyl Cellulose (%)	Wax	Amount (%)	Ethoxy Content	Softening Point (°C)	Viscosity* Centipoises
98	Hydrogenated castor oil	2	47.7	165	59.6
95	Hydrogenated castor oil	5	46.1	159–161	57.9
90	Hydrogenated castor oil	10	43.7	155	49.1
85	Hydrogenated castor oil	15	41.2	145–148	45.0
50	Hydrogenated castor oil	50	24.9	102–105	—
90	Carnauba wax	10	44.2	158–160	—
50	Carnauba wax	50	24.6	120–122	—
90	Montan wax	10	44.5	148–150	—
50	Montan wax	50	26.1	90–93	—
90	Esparto wax	10	43.6	150–153	—
50	Esparto wax	50	24.0	100–105	—
100	none	0	48.4	165–170	70.0

*Viscosity in centipoises determined in a 10 per cent concentration in the mixed solvent of toluene 20, and ethanol 80 parts.

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Chapter 7

Emulsifiable Waxes, Waxy Acids and Metallic Soaps

EMULSIFIABLE WAXES AND WAX STOCKS

Emulsifiable Waxes

An emulsifiable wax is a wax which can be dispersed in water, with or without alteration of its chemical composition. Waxes which contain free alcohols and free acids are emulsifiable, but usually require the assistance of a dispersing agent. Since most of the natural waxes have a low content of free alcohols and acids, and are largely constituted of alcohol-esters and hydrocarbons, preference is given to synthetic waxes which are expressly made for emulsification purposes.

In the emulsification of natural waxes use is made of the fact that a portion of the wax is saponifiable with boiling alkaline solutions; for example, beeswax can be emulsified to an appreciable extent by saponifying it with dilute sodium hydroxide solution.

Some of the emulsifiable synthetic waxes in the worlds market are "Lanette Wax," made in England, "Haftax Wax" (von Hayden A. G.), "Karawax" (K. Himmelbauer, M. Ostrafa, CS. R.), "Nibrenwax" (I. G. Farbenindustrie Aktien-Gesellschaft), "I. G. Wax E" and Emulgier Wax PS (I. G. Farbenindustrie A. G.). Most of these waxes (or those now available) are comprised almost solely of fatty alcohols.

The "glycol waxes," that is the glycol stearates, and related products, are extensively used. These waxes will be referred to later.

Emulsifiable Wax Stocks

The term "emulsifiable wax stock" applies to a wax preparation, conveniently in a form that is water-free or nearly so, and which can be very readily emulsified with water. There are innumerable preparations of this kind on the market for use in compounding polishes, pastes, and leather dressings, for waterproofing paper, etc.

An example of an emulsifiable wax stock is that of Noncle.[15] This stock comprises candelilla wax, gum lac wax, lignite wax, stearic acid, and zinc stearate. For making polishes it is emulsified with a white mineral spirit containing a little ammonia water or an amine, and abrasives are added.

Belt dressings can be made with rosin in combination with wool fat, montan wax, or other emulsifiable wax. Friedrich[7] proposed the treatment of wool fat with an alkali metal at a temperature above 100°, thus excluding the use of water or other solvent. He treated wool fat with metallic sodium for one hour at 150° and obtained an emulsifiable wax-like product. Unsaturated waxes treated with a sulfite and an oxidizing agent, air or oxygen, without the addition of acid, are said to yield water-soluble products.

The principle involved in preparing many of the commercial wax preparations such as metal polishes, stove polishes, pastes, abrasive soaps, polishing creams, etc., is to effect an emulsifying wax combination from hydrocarbons with high molecular weight alcohols, together with a high aliphatic acid or resin acid, the mixture being emulsified with the aid of a dilute alkali. The hydrocarbons can be selected from a group consisting of paraffin, ceresin, ozocerite, or the like; the alcohols from a group consisting of wool-fat alcohols, cetyl alcohol, and mono- or diglycerides; and the acids from stearic, palmitic, etc., or colophony. The alkali is often none other than sodium carbonate, but for many purposes the ethanolamines are preferred. Spermaceti may be effectively used instead of the mineral waxes.

Waxes With Free Alcohols. Typical of an emulsifiable wax which contains free alcohols is *Lanette Wax*, which is substantially a mixture of palmityl and stearyl alcohols. Lanette Wax melts at 50°, and has zero acid and saponification values. The wax is soluble in ethanol, ether, benzene, and many other solvents. Its greatest use in the arts is in the emulsification of water-base compounds—those containing soap, and sulfonated animal, vegetable, or mineral oils. *Rilan Wax*, like Lanette Wax, is used in emulsions for leather dressings, etc. *Karawax* consists of wax alcohols and free fatty acids, and is readily emulsifiable, lending itself to the manufacture of liquid shoe and furniture polishes. It has a saponification gravity of 0.950–0.955 at 15°; melts at 67° to 70°; has an acid value of 17–22, and a saponification value of 44 to 50.

Scale Wax Emulsions. Emulsifiable wax products may be made from *scale wax* (m. 120°–124° F) 88, and petroleum sulfonate (95 per cent) 12 parts; from *scale wax* 88, and petroleum sulfonate (50 per cent) 12 parts; and from *paraffin* (m. 128° to 132° F) 90, petroleum sulfonate (50 per cent) 5, and water 5 parts; also from other combinations of similar material. Such emulsifiable wax stocks when dispersed in water to give an emulsion containing about 5 per cent wax, may be successfully employed in waterproofing paper and cardboard, according to Griesinger.[8] For use in the paper beater the emulsifiable wax stock may be prepared from crude yellow scale wax 85, sulfonate (50 per cent) 15 parts, admixed with a sufficient amount of water to give a 5 per cent wax emulsion. This emulsion is added to the pulp in the beater so that there are 3 pounds of wax to 100 of pulp. The addition of alum solution breaks the emulsion and causes the wax to deposit upon the paper fibers. When the paper is sheeted it will have a low water adsorption power, about 25 to 30 per cent. Paper of this sort has been used in packaging milk and other food products.

Polyhydric Alcohol Fatty Acid Esters. The higher fatty acids such as myristic, palmitic, and stearic acids, invariably form wax-like bodies when combined with a polyhydric alcohol—a glycol, glycerol, sorbitol, or pentaerythritol. Ethylene glycol, $OH \cdot CH_2 \cdot CH_2OH$, commonly called *glycol,* forms with the fatty acids both mono-, and diesters according to the degree of esterification. *Glycol monopalmitate* (m. 51.5°), *glycol monomargarate* (m. 50.2°), and *glycol monostearate* (m. 58.5°) are insoluble in water, and quite soluble in alcohol. *Glycol dilaurate* (m. 50–52°), *glycol myristate* (m. 70.4°), and *glycol distearate* (m. 76–77°) are insoluble in water, and but slightly soluble in alcohol.

Diethylene glycol, $O(CH_2 \cdot CH_2OH)_2$, commonly called *diglycol,* forms both mono- and diesters. *Diethyleneglycol monostearate,* the technical grade of which is referred to as Diglycol Stearate S (m. 56–57°), is dispersible in water and hence extensively used as an emulsifying agent. *Diethyleneglycol distearate,* $(C_{17}H_{35} \cdot COOC_2H_4)_2O$ is also known as *glycostearin* (m. 54–55°). The ordinary wax-like ester of propylene glycol, $CH_2OH \cdot CHOH \cdot CH_3$, is *propyleneglycol monostearate* (m. 48–49°).

The behavior of glycerol, $CH_2OH \cdot CHOH \cdot CH_2OH$, is similar to glycol. The esters in which all three OH groups are in union with the fatty acid are largely met with in vegetable and animal oils, and fats, *e.g.*, glycerol tripalmitate (*tripalmitin*), $C_3H_5(O \cdot CO \cdot C_{15}H_{31})_3$ (m. 65.1°), and *tristearin* (m. 70.8°). The mono- and dihydric esters are, however, obtained artificially and are distinctly waxy bodies. If a terminal OH group of glycerol is replaced by a fatty acid radical, an *alpha* ester is formed. If the adjacent OH group were replaced instead, a *beta* ester would result. Glycerol, 1-monolaurate (*α-monolaurin*) crystallizes in white wax-like needles (m. 63°). Glycerol, 1-monopalmitate (*α-monopalmitin*) crystallizes in leaves (m. 77°), and is moderately soluble in alcohol, *i.e.*, 5.306g in 100g at 22.4°. Glycerol, 1-monostearate (*α-stearin*) crystallizes in needles (m. 81.1°), and is dispersible in water. Its formula is $C_{17}H_{35}COOCH_2 \cdot CHOH \cdot CH_2OH$.

Glycol mono- and distearates, diglycol stearate, glycol laurate, glycerol monostearate, glycerol laurate, diglycol monolaurate, propyleneglycol stearate, and propylene laurate all comprise the commercial glycol and glyceryl esters. The laurates are either liquids or soft solids and are manufactured by esterifying the lauric acid obtained by hydrolysis of cocoanut oil with c.p. glycerin or c.p. glycol. Most of the laurates are faintly alkaline, but *diethyleneglycol monolaurate* as commercially prepared is slightly acid. It is used in varnish removers to retard volatilization of the solvents, as a general plasticizer and softener, and in dyes for carbon papers and typewriter ribbons; also in textile softening, leather finishing, and in cosmetics and polishes. The preparation and uses of the polyhydric alcohol fatty esters have been publicized by the Glycol Products Co., manufacturers of these materials.

d-Sorbitol (1,2,3,4,5,6-hexane diol), $C_6H_{14}O_6 \cdot \frac{1}{2}H_2O$ (m. 89–93°) forms both mono- and di-esters with the fatty acids. The technical grades of *sorbitol stearates* melt within the range of 43 to 56°.

Pentaerythritol *(2,2, -bishydroxymethyl-1,3, -propane diol)*, $C(CH_2OH)_4$, m. 253°, forms several hydric esters with a fatty acid. *Pentaerythritol mono-, di-*, and *tetrastearates* are the better known products. They range in melting point from 47 to 61°, and are used as mold-release lubricants for molded plastic articles prepared from urea-formaldehyde plastic resins. Certain modified fatty acid esters of pentaerythritol and its polymers are known commercially as "Pentawaxes." They can be readily mixed with other waxes, oils, and non-polar solvents, and hence have proved of value in the preparation of polishes.

Glycol Stearate Esters. The most valued ester of the group of glycol stearates appears to be Diglycol Stearate S. One part in 10 to 30 parts of boiling water added to the stearate produces a stable milky emulsion. Suggested uses for Diglycol Stearate S are the lubrication of spring leaves, the extrusion of aluminum tubing, as a lubricant in making collapsible tubes, as a treating agent for paper and cardboard to prevent breakage in stamping and embossing. It can be used as a suspending agent for pigments and abrasives, and hence is useful in making special cleaners, polishes and the like. For cosmetic and pharmaceutical preparations a highly refined grade is used. It is used in conjunction with glycerin or alcohol for hand lotions and creams, which may be perfumed and colored if desired. When incorporated in salves and ointments it is said that stains from the unctuous material are washable. In alcoholic solution it may be sprayed on powders to prevent them from lumping. An ordinary grade of Glycol Stearate S is usable with glycerin in a temporary binder for abrasive powders that are to be later permanently fixed to abrasive and grinding wheels; or which is to be used as a temporary binder for clays prior to firing. *Propylene glycol monostearate* is a neutral light colored wax-like solid which disperses readily in hot water. It is miscible with hot alcohols, hydrocarbons, and oils.

Glyceryl Stearate Esters. The properties of glycerol stearates are quite similar to those of the glycol stearates. The commercial glycerol monostearate in a one per cent aqueous dispersion shows a distinctly alkaline reaction, but it is obtainable finished to an acid condition. The products which may be made with glycerol monostearate include lubricants, plasticizers, waterproofing agents, insulators, polishes, ointments, cosmetics, dental waxes, cooking oils, and fats. Glycerol monostearate is classed as an edible solid, as contrasted to diethyleneglycol stearate. The commercial glycerol monostearate usually contains an appreciable amount of *glycerol distearate.*

Glycerol distearate (*α,α′-distearin*), when prepared from the reaction product of α,α′-dichlorohydrin and sodium stearate, crystallizes in rhombic waxy plates from chloroform. It melts at 79.1°, resolidifies at 76°, is slightly soluble in cold alcohol, but very soluble in hot alcohol. *α,α′-Dipalmitin* similarly prepared from sodium palmitate melts at 72°. The commercial glycerol distearate contains appreciable amounts of α-monostearin, α-monopalmitin, α,α′-dipalmitin, and other glycerides, which cause it to have a relatively low melting point (58° optimum), and make it more dispersible in water. Glycerol distearate is used in shortenings, oleomargarine and other articles of food. In oleomargarine it is said to prevent the seepage of milk. It is also used as an enteric coating for pills and tablets.

Emulsifying Agents

There are a group of emulsifying agents known as the *amine soaps,* which are of great importance in the preparation of emulsifiable wax stocks and technical emulsions. The amine soaps are formed by the reaction of an amine, such as triethanolamine, $N(CH_2 \cdot CH_2OH)_3$, with fatty acid in theoretical combining proportions. With the liquid acids, such as oleic, or coconut fatty acids, the preparation may be conducted at room temperature; with the solid acids, such as stearic acid, it is necessary to melt the fatty acid and the amine (about 1 : 2) together before the reaction will form the addition product, namely amine soap. Emulsions prepared with amine soaps are distinguished by their ease of preparation, small particle size, non-corrosiveness, stability in storage, low alkalinity of their water solutions, and detergent power. Triethanolamine is a viscous liquid with slight ammoniacal odor, very hygroscopic, soluble in water, miscible with polar solvents such as alcohol, but insoluble in non-polar solvents, such as gasoline and benzene. It is not harmful to textiles nor caustic to the skin.

Triethanolamine stearate ("T.E.S.") is a hard, white product that changes to a tan color on aging. It is widely used in the preparation of cosmetics and "pharmacals." The following recipes show how T.E.S. is employed: (1) *Eucalyptus oil emulsion*: eucalyptus oil 75, water 85, and T.E.S. 14 parts. (2) *Paraffin wax emulsion*: paraffin wax 85, and T.E.S. 14 parts. (2) *Paraffin wax emulsion*: paraffin wax 85, water 200, and T.E.S. 10 parts. The oil, or wax, and the T.E.S. are melted together, and the water, which has been previously warmed, is added slowly with rapid agitation, and the stirring continued until the preparation cools.

Monoethanolamine stearate, the fatty acid ester from monoethanolamine $NH_2(CH_2 \cdot CH_2OH)$ and stearic acid, is soluble in hydrocarbon solvents and in mineral oils, and is an excellent cleaning agent. *Isopropanolamine stearate* in the technical grade is a mixture of the fatty acid esters of mono-, di-, and tri-isopropanolamine, and its preferred use is where it is necessary to hold the white color of cosmetic emulsions permanently.

Morpholine soaps are prepared from morpholine, which is an aromatic amine of the formula $O(CH_2)_4NH$. Morpholine has a higher boiling point (128°) than other amines, and is used where it is advantageous to boil the dilute water solutions, or where the dried emulsion film of soap is to have water resistance. Other amine emulsifiers include diethylethanolamine, a hygroscopic liquid which gives fatty acid esters useful in making acid wax emulsions such as those of suspended aluminum formate in water and beeswax which are stable when diluted to 5 per cent wax content.

Ammonium laurate, a tan-colored soft solid, is an excellent emulsifying agent, particularly for the production of oil-in-water emulsions with a high oil content, *e.g.*, mineral oil 65, ammonium laurate 2, and water 10 parts. The oil is warmed and added slowly to the laurate water dispersion, with constant stirring until cool.

Ammonium stearate is a waxy solid which can be dispersed in boiling water to form a stable white paste, or fluid emulsion, by stirring while cooling. It is preferable to sodium and potassium stearates for the purpose. The ammonium stearate is said to be of value in waterproofing cements, stucco and concrete. In preparing the cement for use, a dispersion is first made of the stearate in water (1 : 3) and one half gallon of the paste added to a bag of the dry cement, mixing in the premeasured amount of water. A little ammonia water can be added to increase the speed of setting. Ammonium stearate is used in cosmetics, *i.e.*, in the manufacture of vanishing creams, brushless shaving creams, and similar products. It is used in paste form in the preparation of water-repellent coatings for paper, textiles, and rubber. When dispersed in water it can be applied by spray, brush, or dip methods. On drying, the water and ammonia are drawn off, leaving a water-repellent film.

Ammonium linoleate, a solid which completely melts to a reddish liquid at 75°, is an excellent emulsifying agent. Dutton[2] has described its value in the preparation of a tree wax emulsion that is effective in protecting living trees from sunscald, borer, and fungus injury. The emulsion may be prepared according to the following formula: ammonium linoleate (dissolved in 50 parts of hot water) 3, bentonite (smoothly dispersed in 50 parts of water) 3, paraffin wax 10 parts. The ammonium linoleate solution and the bentonite dispersion are mixed at 70 to 90°, and the molten paraffin wax slowly poured into the hot mixture; the resulting slurry is vigorously stirred until a good emulsion is obtained. When cooled the product is creamy. A recipe for spraying is given as: stock emulsion 36, water 36, aluminum powder 7.2, water to complete 44 parts. Waxes other than paraffin may be used in making the stock emulsion.

Ammonium acid soaps are also used to emulsify oils and waxes. These soaps are *ammonium caprylate, acid* (m. 70°), the *laurate* (m. 80°), *myristate* (m. 75–90°), *palmitate* (m. >100°), and *stearate* (m. 100°, decomposes). The ammonium acid soaps have the general composition $NH_4 \cdot C_nH_{2n-1}O_2 \cdot C_nH_{2n}O_2$, where n denotes the number of carbon atoms in the fatty acid. *E.g., ammonium myristate, acid,* has the formula $NH_4 \cdot C_{14}H_{27}O_2 \cdot C_{14}H_{28}O_2$.

Petroleum sulfonic acid, is finding an important use in the preparation of wax emulsion stocks for waterproofing paper, cardboard, leather, and textile material. The *petroleum sulfonates* employed are oil-soluble sodium salts of sulfonic acids derived in the manufacture of white mineral oil by the sulfuric acid treatment, the sulfonic acids having an acid value of 119 mg KOH per gram. The preparation of the emulsion stock has been described by Griesinger.[8] The ingredients are in the nature of scale wax, which is melted at 200° F together with refined paraffin wax; 3 to 12 per cent of the sulfonate soap is added, and the admixture mechanically agitated while hot. The stock may be formed into cakes, sticks, granules, pellets, flakes, or the like, depending upon the requirements of the user. The emulsifiable stock is diluted with water so that it contains no more than 5 per cent of wax when added to the paper pulp beater. When waterproofing paper stock with the sulfonate emulsion, a sufficient quantity of electrolyte such as alum solution is added to break the emulsion and precipitate the wax upon the paper fibers. After sufficient beating the pulp is delivered to the sheet fabricating machine in the ordinary way. Closely related is the previous discovery that emulsions of waxes for the treatment of fibers or fibrous material may be readily brought about by the use of *amylated naphthalene-sulfonic acid* or *hexalated naphthalene sulfonic acid.*

Synthetic Emulsifiable Waxes

Natural or synthetic waxes of the ester type are heated to not exceeding 200° with a nitrogenous base containing one or more nitrogen atoms and a nickel or cobalt catalyst; the properties of the wax may then be modified by treatment with substituted alkylene oxides such as ethylene oxide, or with epichlorhydrin, etc. The resulting products are useful as soap substitutes, as assistants in the treatment of chemicals, and as emulsifying agents for oils. For example, (1) *beeswax* is heated to 150–160° with ammonia to give a product useful as an ingredient in polishes containing wax; (2) *sperm oil* is heated to 140–150° with ethanolamine containing a little water in paraffin hydrocarbons to form salves; (3) *wool fat* is heated to 160–170° with ethanolamine containing a little water; a product useful for preparing oleic acid emulsions is obtained by treating the product with ethylene oxide at 60–70° in the presence of an aqueous alkali.

The I. G. Farbenind. A. G. held a British patent[10] for separating components, *i.e.* hydrocarbons, acids, and alcohols from waxes such as beeswax, montan wax, and wool fat. The method consists of saponifying the wax, and atomizing the saponified product to convert it into a dry powder, extracting the powder with solvents and acidifying the soaps. This constitutes a step in the further synthesis of waxes of a superior order.

Emulgier Wax PS is the name given to a mixture of hydrocarbons, monocarboxylic acids, alcohols and esters, all of high molecular weight, produced by the air oxidation of a high melting hydrocarbon wax (m. $>$100°) by the Fischer-Tropsch process. The process of air oxidation as it was carried out by the I. G. Farbenindustrie at Oppau (Ludwigshafen) involved the use of a potassium permanganate catalyst, and IG Wax Z as the source of raw material. The oxidation is stopped when the acid value of the product reaches 40 to 45, and the melting point 80°.

Emulgier Wax PS can be readily emulsified in water; it was extensively used in Germany for the preparation of wax emulsions. It was also used as an intermediate in the preparation of waxes used for phlegmatizing explosives. *E.g.*, IG Wax L (see p. 270) and Emulgier Wax PS were heated together to form a ketone (m. 90°), compatible with nitropentaerythritol and RDX explosives (see p. 389).

NAPHTHENATES

Naphthenic Acids

Naphthenes are saturated hydrocarbons containing one or more ring nuclei. The simplest member of these cyclic saturated hydrocarbons is cyclohexane, C_6H_{12}. Naphthenes may have paraffinic side chains attached to the carbon rings. The best sources are the petroleum crudes of California, Venezuela, and Roumania. These crudes also contain naphthenic acids to the extent of 0.1 to 4.0 per cent. In the washing of top oils obtained in the distillation of such crudes these naphthenic acids may be recovered. When top oils are washed with sodium hydroxide, sodium naphthenates are formed, which when separated and treated with sulfuric acid form naphthenic acids and sodium sulfate. The acids are then distilled to purify them.

Although naphthenates have little relation to waxes, they are of interest as one of the by-products in the preparation of paraffin waxes, and as substitutes for some of the liquid waxes used in the preparation of extreme pressure lubricants. Naphthenic acids are fused with metallic oxides for the purpose of producing dryers for paints, enamels, etc. Naphthenates of manganese, cobalt, and zinc are used as driers in paints and lithographic inks. Lead naphthenate is used in extreme pressure lubricants where it is desired to impart a rupture strength of 8000 pounds or more to the sperm or rape oil film. Calcium naphthenate is used in motor oils as a detergent. Copper naphthenate is used in mildew-proofing fabric for sand bags.

WAXY ACIDS

Aliphatic Waxy Acids

Many of the higher molecular weight acids of the fatty acid series $C_nH_{2n}O_2$ are of waxy acid consistency. The better known ones are lauric, myristic, palmitic, stearic, and behenic acids. Although the acids of higher carbon content are even more waxy, they are not easily obtainable for industrial use. The most important of the commercial acids is stearic acid.

Acids from Paraffin

The fatty acids that have been so far directly obtainable from the paraffin waxes are limited to those of lower molecular weight, and comprise those with an odd number of carbon atoms not ordinarily found in fats. For example, Fischer and Schneider[4] heated paraffin and dilute sodium hydroxide at 170° with air under pressure and a catalyst (Fe, Mn and Cu); they obtained a 95 per cent yield of *nonadecanic* ($C_{19}H_{38}O_2$, m. 65 to 66°); *heptadecanic*, ($C_{17}H_{34}O_2$, m. 58 to 59°); *pentadecanic*, ($C_{15}H_{30}O_2$, m. 50 to 51°); and *tridecanic*, ($C_{13}H_{26}O_2$, m. 38°) acids. Paraffins containing not only aliphatic hydrocarbons, but cyclohydrocarbons as well, do produce complexities.

In the process of converting paraffins to the fatty acids the wax mass mixed with a suitable catalyst is subjected to large amounts of air at a prescribed temperature and pressure. After temperature, catalyst and time, the quantity of air used in relation to the unit mass of paraffins has been recognized as the most important variable, according to Pardun and Kuchinka.[16] Grün and Ulbrich[9] in 1923 oxidized a paraffin for 12 hours at 160° using 150 to 1200 liters of air an hour, and concluded that 500 liters of air was the optimum. Pardun and Kuchinka oxidized a paraffin produced in the Fischer-Tropsch synthesis. The wax had a solidifying point of 37° and a saponification gravity of 0.779. The glass apparatus served for oxidizing 50 gram samples and the allowance of air varied from 50 to 2½ liters an hour. The oxidation rate rose toward an optimum as the quantity of air used increased and then levelled off during the whole temperature range in intervals from 100° to 160°. If excessive air flowed through, considerable material was blown out.

Ellis[3] states that in the oxidation of paraffin the waxes used melt at 52 to 57° (the temperatures between 150 and 180°), and that the application of increased pressure speeds up the reaction when air is used as the oxidizing agent. By withdrawing the partially oxidized wax and adding fresh wax to the reaction zone the darkening of the resultant fatty acids may be avoided. Wax acids produced with a 52° melting point wax consist of both fatty and hydroxy acids as well as their anhydrides, lactones, and lactides. The hydroxyacids correspond to the formula $C_{13-17}H_{26-34}OH$-$COOH$. Catalysts of manganese, nickel, chromium, and cobalt result in a higher yield of acids.

Calcium naphthenate has been found to be a good catalyst for the oxidation of petrolatum, under certain conditions of temperature and pressure. Oxidations of paraffin with a naphthenate catalyst can be conducted at 120 to 140°. The reactions can be restrained so as to produce considerable amounts of aldehydes and alcohols rather than acids, as by a patented process using orthoboric acid. A mixture of the crude alcohols had a melting point of 34°. When refined the alcohols had a density of 0.860 at 50°, a melting point of 31.5°, with a low acid number, 0.9. There are quite a number of processes for the industrial production of the so-called wax acids, such as passing the molten paraffin and air concurrently through a multiple-section heated tower.[6]

It has been reported that in Germany fatty acids have been successfully obtained from the paraffin waxes of brown coal. The process employs oxygen-enriched air in the presence of a metal catalyst, with suitable temperatures and pressures. The end products from a representative run are *capric*, *pelargonic*, *lauric*, *undecanic*, and other acids containing from 10 to 18 carbon atoms, or of even greater molecular weight. For practical purposes, the acid mixture is saponified and unsaponifiable residues are returned to the reaction process. To be commercially profitable a highly efficient plant and management are required. It is also reported that when these fatty acids are esterified with synthetic alcohol they have been used as edible fats.

The uses of synthetic fatty acids prepared from paraffin waxes are many. The largest use appears to be in the manufacture of soaps. In insecticide sprays containing kerosene the wax acids are superior to green soap. They are also extensively used in the treatment of lubricating oils.

Acids From Oils and Fats

Fatty acids are marketed as "mixed fatty acids" and "pure fatty acids," or under other suitable designation. The mixed fatty acids may consist of double distilled cottonseed, corn, animal, linseed, soybean, or hydrogenated fish oils. The pure fatty acids are marketed in various types of purity depending upon the source of the raw material and the method of preparation employed. The range of commercial waxy acids is between C_{12} and C_{22}, the C_{14}, C_{16}, and C_{18} acids being by far the more important.

Murmur palm kernel oil provides the richest source of *myristic acid* (36.8 per cent). Palm oil provides the best source of *palmitic acid* (42.5 per cent). Beef tallow provides the best source of *stearic acid* (18.5 per cent).

The solubilities of the pure fatty acids in organic solvents rapidly decrease with a rise in the molecular weight of the acid. For example, the solubility at 20° of *lauric acid* in grams per 100 ml of 95 per cent ethanol is 72.8, of *myristic acid* 15.1, of *palmitic acid* 3.9, and of *stearic acid* 0.9. The solubility of lauric acid in chloroform at 20° is 124, of myristic 48.4, of palmitic 22.5, and stearic 3.8.[1]

The waxy nature of these fatty acids and of their derivatives such as amines, nitriles, ketones, and amides, makes them play an important role in wax technology. The field thus far has been largely in soaps, candles, cosmetics, shaving creams, buffing compounds, soaps, and mechanical rubber goods, but it is being rapidly extended.

Stearic Acid. *Stearic acid* is a whitish crystalline solid in the pure state, and is the C_{18} member of the series of saturated fatty acids having the empirical formula $C_nH_{2n}O_2$. The normal acid therefore has the formula $CH_3 \cdot (CH_2)_{16} \cdot COOH$. Though not a wax, stearic acid is so widely used as a wax in candles, cosmetics, crayons, etc., that it is deserving of being grouped with the waxes. In its crude state it is most often referred to as "stearine."

The name "stearine" is now and then confused with "stearin." Publications are sometimes negligent in retaining the final "e" on the word stearine when they refer to commercial stearic acid. *Stearin* is the fat chemically known as *glyceryl stearate.* Stearin in nature is always accompanied by other glycerides of fatty acids, such as *olein* and *palmitin.* Stearin derives its name from the Greek word for tallow. Stearins include tallow, lard, palm, coconut, and cottonseed-oil stearins.

Stearic acid is prepared by the saponification of stearin, *e.g.*, the stearin may be saponified with alkali and the stearic acid set free from the alkaline stearate by means of a mineral acid, but the shorter and more economical method is to hydrolyze (saponify) tallows or greases by steam or acid as in the processes described below, and then sweat out the stearic acid from the mixed fatty acids by filter-pressings.

The reaction of saponification of stearin yields not only stearic acid but glycerol as well.

$$\underset{\textit{stearin}}{C_3H_5(O\cdot CO\cdot C_{17}H_{35})_3} + 3\,HOH = \underset{\textit{stearic acid}}{3HO\cdot CO\cdot C_{17}H_{35}} + \underset{\textit{glycerol}}{C_3H_5(OH)_3}$$

The gradings produced by the commercial process are designated as *single, double,* and *triple pressed stearic acid.* The term "saponified" relates to the preparatory process. The term "distilled" relates to the subsequent process of distillation that is customarily resorted to when the crude fatty acids are prepared from grease stocks rich in olein and that would otherwise give a low yield of pressed acid. The by-product of distillation is "red oil" which is a technical grade of oleic acid.

The natural color of saponified grades of stearic acid is a pale amber, and this is preferred by crayon manufacturers and certain others to the whiter distilled grade because of its harder texture.

The gradings are designated according to method of manufacture—namely, as single, double, and triple pressed stearic acid. The terms "saponified" and "distilled" relate to the processes involved in manufacture. All stearic acid is saponified, and distillation when employed is a subsequent operation separate and distinct from saponification. The The natural color of the saponified grade is a light amber, and because of its harder texture and lower content of palmitic acid it is preferred to the distilled grade by crayon manufacturers and certain others.

Greases or tallows may be hydrolyzed into fatty acids by treatment with steam in a high pressure autoclave, or in an open vat by steam boiling with sulfuric acid and a catalyzer, known as Twitchell reagent. The resulting fatty acids contain a large amount of oleic acid (red oil). The following description is that of Blake, and represents the process as conducted at one particular plant.

The first operation is a washing, carried out in large wooden tanks equipped with open steam coils. Crude grease is run in, dilute sulfuric acid added, and the mixture is cooked with live steam for 1½ hours. The principal purpose of this operation is the removal of mechanical impurities. The charge is then run to another steam tank, where saponification is carried out. The Twitchell reagent is added here and the stock boiled for 18 to 20 hours, at the end of which time the "sweet water" containing the glycerol obtained as a by-product is run off.

A so-called second boil follows, and the crude fatty acid stock, free from glycerol, is again cooked in the tank employed for the original saponification. This treatment raises the fatty acid content to around 97 to 98 per cent. If the grade of grease employed requires distillation in addition, the fatty acid mixture from the second boil is transferred to the distilling department; but if the saponified grade is being prepared, the charge is sent directly to the storage tanks in the cold press department. For distillation a typical fatty acid still is used, which is copper-lined and operated with superheated steam under vacuum. The distillate is a highly refined fatty acid mixture, running a little less than 50 per cent of stearic acid, and the residue in the still is the material known as stearin pitch.

The crude fatty acid in the melted state is piped into pans and allowed to cool and solidify. The cakes thus formed are wrapped in cloth and pressed in a large hydraulic cold press. The first pressing requires about 2½ hours and produces a low grade material. Further removal of oleic acid is required; this is accomplished by pressure under elevated temperature conditions.

The cold-pressed acid is melted and again cascaded into pans and formed into cakes, which are wrapped in coarse cloth in preparation for hot pressing. The conditions of operation govern the grade of the final product.

Triple-pressed stearic acid is subjected to two hot presses—the first for 3 to 3½ minutes, and the second for 5 to 6 minutes with steam of 120 pounds of pressure continuously circulating through the press. Double-pressed acid receives one hot pressing, which is of relatively long duration. Single-pressed acid of standard rubber grade is also hot-pressed, and differs from the double in that the period of hot-pressing is shorter, namely, 3 minutes instead of 5. Each grade is melted and boiled with sulfuric acid in a large tank to improve the color. The product is drained while hot and is finally cascaded into pans which serve as molds to form slabs of finished product.

Single-pressed stearic acid contains about 15 per cent of oleic acid, double-pressed 9 per cent, and triple-pressed 2 to 4 per cent. All grades contain over 45 per cent of palmitic acid, and less than 3 per cent of myristic acid.

Hydraulic pressing and simple distillation in cast iron pot stills have been the only methods of consequence employed in the production of fatty acids, but more recently a third method, a fractional distillation process has been the means of marketing superior grades of fatty acids. If in addition to the distillation a hydrogenation procedure is utilized, acids such as *arachidic* and *behenic acids*, which rarely occur in nature, can be produced. This new technique of fractional distillation of fatty acids, according to Stingley,[17] has opened up an entirely new field of aliphatic chemistry as the pure acids produced furnish a means of making a myriad of derivatives for application in every field of chemistry. Stingley has tabulated the characteristics of the new commercial fatty acids as compared with the chemically pure fatty acids.

There have been many attempts to convert the by-product "red oil" into candle material by Hausamann, Hartl, Shuoff, Gray, Magnier, de Hemptinne, Böhringer, Petersen, Fokin, and others. Generally speaking such processes have involved some scheme of treatment with sulfuric acid, with or without the aid of an electrical current, whereby the oleic acid is

Comparison of Chemically Pure and Commercial Fatty Acids

	Caprylic Acid $C_7H_{15}COOH$	Capric Acid $C_9H_{19}COOH$	Lauric Acid $C_{11}H_{23}COOH$	Myristic Acid $C_{13}H_{27}COOH$	Palmitic Acid $C_{15}H_{31}COOH$	Stearic Acid $C_{17}H_{35}COOH$
Chemically Pure Fatty Acids						
Mean Molecular Weight	144.12	172.15	200.19	228.22	256.25	284.28
Melting Point	16.5°	31.3°	43.6°	53.8°	62.85°	69.9°
Iodine Value (Wijs)	none	none	none	none	none	none
Neutralization Value	389.0	326.0	280.0	246.1	219.0	197.0
Unsaponifiable Matter	none	none	none	none	none	none
Color	water-white	white	white	white	white	white
New Commercial Fatty Acids						
Mean Molecular Weight	145.7	173.3	203.0	226.0	258.0	282.5
Melting Point	13.0°	30.0°	37.8°	51.0°	58.0°	67.0°
Iodine Value (Wijs)	0.8	1.0	1.0	2.0	3.0	3.0
Neutralization Value	385.0	323.7	276.0	248.0	216.0	198.0
Unsaponifiable Matter, %	trace	0.5	0.4	0.2	0.5	0.5
Color	water-white	white	white	white	white	white

converted to a solid compound. Lewkowitsch in 1907 was the first to practically apply the Sabatier and Sendersens synthesis in reducing the oleic acid quantitatively to stearic acid by means of hydrogen in the presence of finely divided metals.

Properties of Stearine. Stearine melts at 52 to 56° (125.6 to 132.8° F). This melting point is much below that of the chemically pure stearic acid. It has a neutralization value of 205 to 207, and a saponification value of 206 to 208. These values are considerably higher than those of the pure acid. Stearine contains a considerable amount of the C_{16} fatty acids, some myristic and oleic acids, and 0.3 to 0.5 per cent of hydrocarbons. The specific gravity of stearine is 0.850 at 15°. It boils at 383°. Its refractive index at $\frac{80^\circ}{D}$ is 1.4299. Stearine is used in the manufacture of the water emulsified types of shoe creams and polishes, since it is amenable to partial or complete saponification as desired.

U.S.P. Stearic Acid. The United States Pharmacopœia describes a stearic acid which is well suited for pharmaceutical use. A review of the U.S.P. specifications will soon show that U.S.P. stearic acid contains a very large proportion of palmitic acid. U.S.P. stearic acid, or "acidum stearicum," is described as a hard, white or faintly yellowish, somewhat glossy and crystalline solid or a white or yellowish-white powder. The odor and taste are slight, suggesting tallow. Stearic acid is insoluble in water. One gram of U.S.P. stearic acid dissolves in 21 ml of ethanol, in 2 ml of chloroform, and in 3 ml of ether, at 25°. In the tests for purity the U.S.P. states that the congealing temperature should not fall below 54° (129.2° F) nor the iodine number exceed 4. Tests are also described as to how to detect mineral acid, neutral fat or paraffin as impurities.

The author determined the melting point of a specimen of U.S.P. stearic acid furnished by a leading chemical supply house in New York, as 55.8° (132.5° F). The specimen was pure white and had a splendid crystalline structure. It contained 40 to 45 per cent of palmitic acid. The durometer hardness was 95 at 34° F, and 92 at 82° F. It is of interest to note that the hardness of stearic acid does not vary greatly over a wide range of temperatures. The iodine number was 2.

Triple-Pressed Stearic Acid. An acid as above described can be easily identified as a triple-pressed acid from its relatively high melting point, and low iodine number. If the acid were "double-pressed" the melting point would be 54 to 54.5°, and the iodine number 7 to 9 instead of 2 to 4. A single-pressed acid would melt at about 53°, and would have an iodine number of 10 to 14. Each successive pressing removes a considerable quantity of the liquid fatty acids and reduces the amount of unsaponifiable material. It is customary in the refinery to melt down pressed stearic acids and boil them with sulfuric acid to improve their color. The product is drained hot, and finally drawn off through pipes and again cascaded into pans which serve as molds to form the slabs of finished product.

Vacuum Distilled Stearic Acid. Armour & Co. offer a vacuum distilled c.p. stearic acid under the designation "Neo-fat No. 165". This stearic acid has a melting point of about 67° (152.6° F). The acid contains 90 per cent of stearic, 6 per cent of palmitic, and 4 of oleic acid. It has an iodine number of 3.0 (Wijs), and an unsaponifiable content of 0.5 per cent. A specimen examined by the author had a melting point of 66.7° (152° F); softening point of 66.7; durometer hardness of 68 at 34° F, 75 at 75° F; and a specific gravity of 0.9088 at 25°/15°, and 0.9145 at 5°/15°.

Depression of Melting Point. The influence of palmitic acid in depressing the melting point of stearic acid has been shown by Heinz. The melting and solidifying points are given here for the palmitic acid content (0 to 100 per cent) of a mixture of the commercially pure acids.

Percentage of Palmitic Acid	Melting Point (°)	Solidifying Point (°)
0	69.2	—
10.0	67.2	62.5
20.0	65.3	60.3
30.0	62.0	59.3
40.0	60.3	56.5
50.0	56.0	55.0
60.0	56.3	54.5
67.5	55.2	54.6
70.0	55.1	54.6
80.0	57.5	53.8
90.0	60.1	54.5
100.0	62.0	—

Lewkowitsch[12] states that the mixtures of pure fatty acids are apt to form "eutectic" compounds, behaving as regards melting and solidifying points like pure chemical substances. Thus a mixture of 47.5 per cent of stearic and 52.5 of palmitic acids behaves as a chemical unit and cannot be resolved into its components by crystallization from alcohol. The eutectic of the mixed acids has a solidifying point of 54.50°, whereas the pure palmitic acid melts at 62.6° and the stearic acid at 69.3°. Recent evidence exists that the eutectic crystal phase may be bimolecular—that is, the palmitic acid and the stearic acid linked by free hydrogen atoms—and also that the individual acids can to a certain extent be bimolecular.

Hardness of Stearic Acids. For many purposes it is desirable to use a hard grade of stearic acid, even though the melting point is somewhat lower than in the purest grades. Of the fatty acids, oleic and myristic lower the hardness of the commercial stearic acid, and palmitic acid greatly increases it. Hence the presence of palmitic acid to the extent of 20 to 40 per cent is not objectionable, provided the oleic acid content is below

4 per cent. The following figures are based upon specimens of stearic acid having 3 to 4 per cent of oleic acid and varying amounts of palmitic acid, resulting in almost a straight line curve when plotting durometer hardness against the percentage of palmitic acid. The data are taken from such a curve.

Percentage of Palmitic Acid	Durometer Hardness at 4.4°
6	66
10	68
15	70
20	73
25	76
30	80
35	84
40	89
45	94

Myristic acid of 90 per cent purity has a hardness of 54 at 4.4°.

Pure Stearic Acid. The preparation of very pure stearic acid from natural sources presents many difficulties, and hence synthesis must be resorted to. Various methods have been proposed to convert commercial grades of stearic acid to the chemically pure standard; *e.g.*, the addition of a little magnesium acetate to a concentrated alcoholic solution of fatty acids, whereby the salts of the higher fatty acids (stearic acid) which are soluble in alcohol with difficulty are precipitated. Another method is based upon the fractional distillation of the fatty acid esters; and a third on fractional neutralization with alkalies, the lower fatty acids being neutralized before the higher.

The greater solubility of palmitic acid in ethanol can be taken advantage of to remove palmitic acid, and to prepare a stearic acid of plus 95 per cent purity. In absolute ethanol the solubility of palmitic acid is 31.9 grams per 100 ml, whereas that of stearic acid is 13.8 grams per 100 ml. Bulatkin[18] prefers to use c.p. ethyl acetate at a constant temperature of 37°. In this method 350 grams of "double-pressed" stearic acid were dissolved in 350 of ethyl acetate in a flask, and the contents of the flask heated to 70° until all of the stearic acid dissolved. The flask was capped with metal foil and placed overnight in a constant temperature oven where the temperature was maintained at 37°. The stearic acid residue was separated from the solvent, drained and dried. The residue after making a melting point determination was again taken up with an equivalent weight of solvent and the process repeated. Five treatments resulted in a stearic acid m. 64°. The successive melting points were 54.5° (original), 55.5°, 57°, 58°, 59° and 64°. Further treatment is required to obtain an acid approaching a 69° melting point.

Hydroxystearic Acid. Hydroxystearic acid, prepared by hydrogenating ricinoleic acid of castor oil, is produced on a commercial scale. It is therefore the Δ-hydroxy- or 12-hydroxystearic acid. In its crude commercial form it is a tan-colored, hard wax, m. 77 to 79°. It has a viscosity of less than 50 centipoises at 85°. The acid has a neutralization value of 185. It is compatible with paraffin wax, beeswax, carnauba wax, candelilla wax, and stearic acid. It is insoluble in water; soluble in hot ethanol, partially soluble in cold ethanol; soluble in hot naphtha, from which it gells on cooling; and soluble in hot toluene, from which is also gels on cooling.

Stearyl Hydroxystearate. Hydroxystearic acid is esterified to produce a stearyl hydroxystearate. The hydroxystearic acid is of the kind described above, and the stearyl alcohol used in the esterification is one having a melting point of 54 to 57°, and distillation range of 300° to 375°, a hydroxyl number of 215, and an iodine value of less than 2. Stearyl hydroxystearate is a hard wax, tan in color, melting at 69 to 72°, viscosity less than 50 centipoises at 75°. The commercial wax has a specific gravity of 0.900 at 25°, and 0.839 at 75°, and a coefficient of expansion similar to paraffin wax. Its solubility characteristics are like those of hydroxystearic acid. Although compatible with waxes and resins when hot, it tends to separate on cooling.

Uses of Stearine and Stearic Acid. The rubber manufacturers are large users of stearine and stearic acid and purchase it under specifications involving (1) melting point or titer; (2) iodine absorption value (Hanus number); and (3) percentage of free fatty acid. Double-pressed distilled grade is used by the candle makers, but single-pressed is satisfactory for most rubber compounding. The function of stearic acid in rubber is to stabilize the cure, activate an accelerator, to increase workability, and to facilitate mold release. It is also used as a softener for rubber.

Stearine has an important place in the reclaimed rubber industry. It does not compare favorably with other softeners in plasticizing efficacy when used in contact with vulcanized rubber scrap during vulcanization; but when added as a softener it does make the reclaimed batch more plastic, improves tubing and calendering properties, reduces nerve without production of excess "talk," improves tensile strength, modulus, and molding properties of reclaimed rubber, and helps to disperse the pigment.

Stearine is also used in the preparation of hard greases, such as "journal greases." It is used to lubricate the molds in the molding of plastics. Triple-pressed stearic acid is used in shaving creams, cosmetics and pharmaceutical preparations.

About 30 per cent of the stearic acid entering commerce is used by the rubber manufacturers, and the production of all grades exceeds 50 million pounds per annum. Fatty acid manufacture consumes 15 per cent of all the grease produced; the rest goes to the soap industry.

METALLIC SOAPS

The alkaline earths and the heavy metals form with the fatty acids insoluble soaps, most of which are waxy. The inorganic bases of these insoluble soaps include calcium, magnesium, barium, aluminum, zinc, lead, copper, cobalt, and nickel. The fatty acids include lauric, myristic, palmitic, stearic, oleic and erucic.

Preparation of Metallic Soaps. The method of preparation may be dry or wet. In the wet method the fatty acid is weighed out and dissolved in hot ethanol, then exactly neutralized with dilute sodium hydroxide in the computed mole weight plus one per cent. The bulk of the ethanol is evaporated off, water added, and the metal salt such as the acetate added slowly with stirring. The double decompositions are best conducted at 60°. The precipitate of metallic soap is allowed to stand and then filtered, washed with water and ethanol, and then dried in a spread condition at about 60° for the *laurates* and *myristates*, or at 75° in a vacuum oven for *palmitates*, *stearates*, and higher fatty acid salts.

The technical methods of preparation of the metallic soaps generally use steam for melting the fatty acid, and after the sodium hydroxide has been added, the temperature is dropped from about 90° to 75° and the metal salt very slowly added. The slurry formed is kept hot by steam and filtered at 85°, and the metallic soap dried in a vacuum oven. An alternative method is to dissolve the sodium hydroxide in water, heat to 90°, and pour in the melted fatty acid while mechanically stirring.

In the dry method of preparation a preferred procedure which can be generally applied to the heavy metals, as well as the alkaline earths, is one in which the fatty acid is melted with the mole equivalent plus a slight excess of the powdered hydroxide of the metal. The resultant metallic soap is washed with water and ethanol to remove impurities.

Physical Constants of Metallic Soaps. The soaps of the alkaline earths, namely calcium, magnesium, strontium, and barium are white crystalline powders, which when fused by heat become plastic, and on cooling congeal to more or less brittle frits. The glassy masses of the magnesium soaps are yellow, alike in appearance, but differing in hardness. The durometer hardness of *magnesium myristate* is 42, *pamitate* 62, and *stearate* 84, at 25°. The stearate is quite tough, the palmitate somewhat brittle, and the myristate fragile. *Calcium stearate* is a trifle harder than magnesium stearate. *Calcium palmitate* is very hard. The laurates and myristates of the alkaline earth metals have an unctuous texture, whereas the palmitates, and higher metallic soaps are distinctly waxy. Aluminum, zinc, and cadmium salts of the fatty acids are also white, fluffy powders as prepared by the wet method.

Many of the heavy metal soaps are highly colored. *Copper soaps* are turquoise blue; *nickel soaps* bright green (laurate) to olive green (stearate); *silver soaps* buff; *cobalt soaps* violet blue; *tin soaps* gray; *chromium soaps* pale drab gray; and *iron soaps* yellow-brown in color.

The melting points of the metallic soaps are for the most part indefinite; a few that are well defined are fatty acid salts of lead, zinc, and mercury. The drop points of most of the metallic soaps are so high because of the gels they form, that a method such as the "straight tube capillary" must be resorted to in order to determine the temperature of transition between the solid and the fluid state.

The transition of solid-fluid-solid of the metallic soaps involves four stages. In stage *1*, the softening point, gelation begins. In stage *2*, the gelation point, the gelation ends. In stage *3*, the liquefying point (so-called melting point) the gelate liquefies. In stage *4*, the crystal point of Lawrence[11], the gelate crystallizes to a hard solid. The frits obtained from melting powdered soaps, which have been prepared by the wet method, will in many instances melt at a lower temperature than the original powders, possibly because of a smaller unit crystal cell structure.

Approximate Melting Points of Pure Metallic Soaps

	Mg.	Ca	Ni	Zn	Hg	Pb	Cu
C_{12}	82.0°$^{(3)}$	108.0°$^{(3)}$	77.0°$^{(3)}$	128.0°$^{(1)}$	100.0°$^{(1)}$	106.0°	112.0°$^{(1)}$
C_{14}	86.8°$^{(2)}$	112.0°$^{(3)}$	85.0°$^{(3)}$	129.0°$^{(1)}$	102.0°$^{(3)}$	110.0°$^{(1)}$	116.0°$^{(?)}$
C_{16}	99.0°$^{(2)}$	122.0°$^{(3)}$	96.0°$^{(3)}$	130.0°$^{(1)}$	105.0°$^{(1)}$	113.0°$^{(1)}$	120.0°$^{(1)}$
C_{18}	107.0°$^{(2)}$	140.0°$^{(2)}$	100.0°$^{(1)}$	132.0°$^{(1)}$	112.2°$^{(1)}$	115.0°$^{(1)}$	125.0°$^{(1)}$
C_{24}	140.0°$^{(?)}$	———	———	134.0°$^{(1)}$	———	117.0°$^{(4)}$	———
C_{26}	150.0°$^{(3)}$	160.0°$^{(3)}$	112.0°$^{(3)}$	138.0°$^{(3)}$	115.0°$^{(3)}$	118.0°$^{(?)}$	126.0°$^{(3)}$

$^{(1)}$ Melting points by Whitmore and Lauro[20], $^{(2)}$ by Warth and Hanzely,[19] $^{(3)}$ by Warth and Bulatkin,[18] $^{(4)}$ by Lewkowitsch.[13] The fatty acid radicals listed as C_{12}, C_{14}, ... are those of laurates, myristates, palmitates, stearates, lignocerates, and cerotates respectively.

The technical grades vary greatly in their physical characteristics from those of the pure metallic soaps. This may be attributed to the use of raw materials of technical grade, the method of preparation, and the objective of manufacturing soaps of specific properties for industrial use. The technical soaps are rated as to appearance, softening point, content of metal as oxide, water-soluble salts if any, bulk in fluid ounces per pound, acetone extractable, and water content. The Mallinckrodt Chemical Works list the following softening points (viscous mass to the near liquid stage) for the technical grades of metallic soaps: *aluminum monostearate* 190–200°; *aluminum distearate* 155–160°; similar but "fluffy," 145–150°; *magnesium stearate* 125–130°; *sodium stearate* 180–185°; *zinc stearate* 112–117°; similar but U.S.P. XII quality, 112–117°.

The metallic soaps when blended in small amounts with paraffin and other waxes increase the melting point, produce a fine grain structure, increase ductility and tensile strength, and improve moisture repellancy. Large amounts of the metallic soaps are usually not compatible with paraffin without the addition of some stearic acid. In preparing emulsions of wax with water, acidulated compounds (anilides, toluidides, etc.) of the heavy metal soaps can be blended with crude scale wax as an emulsifying stock.

Uses of Metallic Soaps. Calcium stearate powder (s.pt. 150°) is very soft and bulky, of relatively high melting point, insoluble in oils and waxes, and inert to solvents; hence its inability to gel. It is recommended as a releasing agent for the plastics molding industry, and as a flatting agent for paints, varnishes, and lacquers. It is used in floor polishes, waterproofing fabrics, and in crayons. The best of the grades is used to lubricate the metal parts employed in the manufacture of compressed candies. *Magnesium stearate* (s.pt. 130°) is soft and bulky, insoluble in cold but soluble in hot alcohol. Its smooth bulkiness and efficient covering and bodying action make it widely useful. It is used in the manufacture of cosmetics and ointments; in paraffin-oil slushing compositions for lubricating dies used in extruding, molding, compressing and stamping operations. It is used as a flatting agent for varnishes; and as a rubber ingredient. *Aluminum monostearate* (s.pt. 200°) is soluble or dispersible in nonpolar solvents, oils and waxes. Such solutions or dispersions are gelled and stay gelled upon cooling. It resists wetting with water. It takes but 1 or 2 per cent of aluminum monostearate to harden a lubricating grease. *Aluminum mono-palmitate* is used in plastics, wire drawing, waterproofings, and coated papers. *Aluminum distearate* (s.pt. 160°) is insoluble in water, lower alcohols, ketones, and esters; it is decomposed by boiling methanol or ethanol. It has a pronounced gelling action with oils and greases, and hence is used to thicken them. It is also used as a flatting agent for paints and varnishes, as a waterproofing agent for paper, textile fabrics, rope, and structural materials, or wherever a high gel strength is required. *Lithium* stearate (m. 136°) toughens paraffin wax, raises its melting point and tensile strength; lithiated paraffins are dust repellant and form suitable ingredients with carnauba wax in polishes. Lithium soap greases are of value in lubricating bearings that operate at high temperatures. *Zinc stearate* of a U.S.P. grade is commonly employed in dusting powder for skin diseases and in baby dusting powders. Zinc stearate lacks gelling power; and makes a good flatting agent for nitrocellulose lacquers; it is also used as a constituent of sanding lacquers, and sealers. *Copper stearate* is used in antifouling paints and in fungicides. *Strontium stearate* has been suggested for pyrotechnic flares and signals since it burns with a scarlet flame. *Mercury* and *lead* salts of the fatty acids are used in medicinal ointments. *Nickel* soaps have been suggested as catalytic agents to promote intimate contact between catalyst and oil in the hydrogenation processes.

'WAX EMULSIONS FOR SPECIFIC USES

Anti-Freeze Wax Emulsions

It is a common practice to employ material in automobile radiators to prevent the freezing of the water at low temperatures. Some of the more desirable anti-freeze agents are glycerin, ethylene glycol, diethylene glycol, and other similar alcohols. These agents have a tendency to foam in use, and Flaxman[5] has proposed an anti-foaming wax base composition that can be added to the glycerin, or similar agent. *Montan wax* which has been partially saponified is dissolved in lard oil or mineral oil to the extent of 1 to 5 per cent. The anti-foaming agent may be prepared from water 20, montan wax 4, potassium hydroxide (dry) 0.25, and glycerin 25 parts. The wax is added to most of the water; the KOH in solution in the rest of the water is slowly added. The mixture is brought to boiling. After 20 to 30 minutes of boiling the glycerin is stirred in and the mass agitated at about 93° (200° F) for 10 minutes and then cooled. The boiling brings the glycerin content to about 60 per cent. There must be no excess of KOH after saponification. The cooled mixture is then admixed with 50 parts of lard oil, castor oil, or mineral oil of appropriate consistency.

A good formula for a concentrated anti-freeze solution containing the foam-preventing agent would be the following: Water 20, glycerin 79, lard oil 0.5, anti-foam agent, as first described, 0.5 parts. The water is charged into a kettle and about 10 per cent of glycerin mixed therein. About 25 per cent of the anti-foam agent is stirred in, and the remainder of agent and lard oil are then added slowly with rapid agitation. About 0.1 per cent of sodium silicate is added and the anti-freeze product packaged for use.

Emulsions for Finishing Fibers

Waxes that cannot be classified as emulsifiable can nevertheless be emulsified by dispersing them in highly emulsifiable chemical agents. For example, 10 parts of ammonium linoleate are added to 500 of water; to this mixture 50 parts of melted carnauba wax are added. Such an emulsion has been suggested by Muller[14] for finishing furs, such as lambskins, etc. The furs to be treated are immersed in a solution comprising carnauba wax emulsion 20, aluminum formate 20, phthalic acid 20, ethyl lactate 10, formaldehyde 30, and water 900 parts. They are then hydro-extracted, roughly dried at 100 to 120° F, and flashed at 240 to 250° F, brushed and ironed.

Crude scale wax can be emulsified with stearic acid and ammonia water at 123 to 125° F. For example, such a composition is used for surface treating hemp or other vegetable fibers which are fabricated into rope to make the fibers resistant to wear and the deterimental effects of water.

Refined wool wax and commercial *beeswax* are emulsified directly with ammonia water, as: wax 10, strong ammonia, water (26° Bé) 3, and water 87 parts. Crude scale wax emulsions are preferred because of their cheapness.

Suitable wax finishes are marketed for laundered fabrics such as women's wear, curtains, sleeping bags, uniforms, sports clothes, rainware, childrens clothes, etc.

Wax Finishes for Metal

Rust inhibiting wax emulsions are made in the clear and black colors for finishing hardware, padlocks, stovepipe, kitchen utensils, garden tools, bolts, screws, typewriter and camera parts, etc. The finish protects metal surfaces against corrosion, provides a dry lubrication, and adds to the appearance and beauty of the object coated. Wax finishes are also produced to enhance the beauty of plastic objects.

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Chapter 8

Methods for Determining the Constants of Waxes

DETERMINATIONS OF CHEMICAL CONSTANTS

Significance of Chemical Constants

Chemical constants are determined in order to identify, differentiate, or classify the waxes. The *saponification value,* also referred to as the *saponification number*, is characteristic for most waxes. The term "number" is more often used to express the value of a specific constitutent in a fat or wax. The *acid value* expresses the free fatty (or waxy) acid, and is more of a variable than the saponification value. The *ester value* is generally regarded as the difference between the saponification value and the acid value. It is quite often, but not always, a measure of the amount of ethers or esters in the wax.

When a single acid constituent of a wax is considered, where the acid value and saponification value are substantially one and the same thing, the amount of alkali (KOH) required to effect neutralization is referred to as its *neutralization number,* and this number can be calculated if the molecular weight of the acid is known, by the formula:

$$\text{Neutralization number} = \frac{56{,}104}{M}$$

E.g., ursolic acid, $C_{29}H_{46}(OH) \cdot COOH$, has a molecular weight of 456.68; hence its neutralization number is

$$\frac{56{,}104}{456.68} = 122.85$$

A specimen of the commercial ursolic acid had an acid value of 121.5 and a saponification value of 123.5 by actual analysis.

The *non-saponifiable* matter is an important determination in the identification of a wax. It includes not only the *unsaponifiable* portion of wax but also combined *alcohols* split off from the ethers or esters, as well as the *free alcohols* and the *hydrocarbons* present. The percentage of total fatty or waxy acids is approximately the difference between the percentage of non-saponifiable matter and 100 per cent.

The principal differences to be expected in the analysis of a wax are:

(1) in the mean molecular weight of the acids present or the relative proportions of acids of high and low molecular weight; (2) in the relative number of double bonds depending upon the proportion of acids of the saturated and unsaturated types; (3) in the proportion of alcohols present, and in some instances the proportion of hydroxyacids present; (4) in the proportion of esters of the higher fatty acids, or of free fatty acids; (5) in the proportion of hydrocarbons present.

The constants most often used may be grouped as follows: (1) saponification value, and occasionally the Hehner number and Reichert-Meissl number; (2) halogen absorption number; usually Hübl iodine number, or Hanus iodine number; seldom the Maumené number; (3) acetyl number as a measure of hydroxyl groups, alcohols, hydroxy acids, and sterols; (4) acid value, and indirectly the ester value; (5) the hydrocarbons in percentage amount, determined by extraction of the unsaponifiable matter and ultimate analysis for carbon and hydrogen.

Chemical tests other than those mentioned above are sometimes made for the identification of the constituents of a wax, *e.g.*, tests for: (1) thiocyanogen (CNS_2) absorption and the formation of crystalline bromo-addition products; (2) the proportion of water-soluble or -insoluble volatile-fatty acids present; (3) the analysis of small amounts of glycerol; (4) the analysis of small amounts of resins, including colophony; (5) the presence of sterols (quantity, if possible); (6) the presence of lactones (quantity, if possible); (7) the presence of mineral matter, and whether it is free or combined.

Saponification Value. The saponification value is the number of milligrams (mg) of potassium hydroxide (KOH) required to hydrolyze one gram (1 g) of the wax or waxy material.

The determination of the saponification value (sapn. val.) of a wax follows the procedure of an oil, except that the solvent selected for the purpose must be one that will keep the unsaponifiable portion in a state of solution, and hence for some waxes alcohol of 96 per cent strength, or even absolute alcohol, cannot be safely used.

For the ordinary determination of the saponification value it is customary to take 2 to 5 g of sample, and insert this in a 250 to 300 ml flask containing 30 ml absolute alcohol. Alcoholic KOH (50 ml of approximately half-normal, or 25 ml of approximately normal) is run from a burette with constant stirring at a steady rate, say for 2 minutes. The contents of the flask are gently boiled with occasional thorough shaking for at least one hour after the solution starts boiling, under a reflux or air condenser, plugged at the top with glass wool. The excess of KOH is titrated with half-normal ($0.5N$) or tenth-normal ($0.1N$) hydrochloric acid (HCl). In addition to phenolphthalein as an indicator it is a good plan to add 1 ml of methylene blue (0.1 per cent strength) so that the end point is more sharply distinguished by transition from a brownish-purple or bluish-purple to a clear pale or dark green color.

Converting the normality of the HCl to that of normal KOH:

$$\text{Saponification value} = \frac{(v_b - v_w) \times 56.104}{w}$$

Where w = weight of sample taken, and v_b, v_w are respectively number of milliliters of normal HCl used in the blank and the actual analysis.

In determining the saponification value of beeswax a more concentrated solution of KOH has been favored and an extension of the time of saponification; *e.g.*, 3.5 g of wax are dissolved in a minimum of absolute alcohol and 35 ml of 0.5*N* KOH added, and the saponification carried out for 3 hours.

Marcusson preferred to use benzene with montan wax.

Berg dissolved carnauba wax in xylene. Berg's method specifies that 4 g of the wax sample are dissolved in 20 ml of xylene, then 50 ml of 0.5 *N* alcoholic KOH are added and the solution boiled for 2 hours under a reflux condenser. Next, 100 ml of alcohol are added and the solution titrated with 0.5*N* HCl. Berg found this procedure more effective than boiling for 8 hours or more with alcohol as the solvent. A modification of the Berg method is in use for determining the acid and saponification values of carnauba and other waxes, namely: Boil 4 g of wax with 20 ml of absolute alcohol for 5 to 10 minutes with reflux, and titrate the hot liquid at once with 0.5*N* NaOH for acid value. Add 50 ml of 0.5*N* alcoholic KOH, boil for 30 minutes, add 75 ml of 96 per cent alcohol, heat 5 minutes, titrate with 0.5*N* HCl, boil 5 minutes and again titrate until colorless for saponification value.

Toluene is preferred by Wand[4] as the solvent for the wax sample, because of its great solvent power and its miscibility with alcohol. The procedure is as follows: Place 2 g of the wax in a dry 250 ml Erlenmeyer flask. Measure in exactly 10 ml of pure toluene. Warm gently on hot plate until wax dissolves but do not boil. Now run in from a pipette 25 ml of 0.7 *N* alcoholic KOH (approximately 39 g of KOH per liter). At this point some of the dissolved wax may precipitate but it will redissolve when the flask is warmed. A blank determination is run by measuring the same amounts of toluene and reagent in a second flask. Place both flasks under reflux condensers and hold at a gentle boil for 2 hours, to complete the saponification. Now add 5 to 6 drops of phenolphthalein indicator and titrate to complete disappearance of pink. The blank, containing 25 ml of alcoholic KOH will require 35 ml of 0.5 *N* HCl. The difference between the blank and the sample measures the amount of KOH consumed in the saponification. 1 ml of 0.5 *N* HCl is equivalent to 28.06 mg of KOH.

Amyl alcohol can be used to advantage where it happens to be a formidable solvent for the end products of saponification that cannot otherwise be kept in solution. Isopropyl alcohol may be used in place of amyl alcohol.

Saponification Equivalent. The saponification equivalent is the amount of fat or wax saponified by one gram-equivalent of KOH, and is therefore the mean gram-equivalent of the mixture of glycerides or of wax esters, as the case may be, in the material examined, on the assumption that the latter consists of neutral and not acid types.

$$\text{Saponification equivalent} = \frac{1000w}{v_b - v_w}$$

$$\text{or,} = \frac{56{,}104}{\text{sapn. val.}}$$

Acid Value. The acid value is the number of milligrams of KOH required to neutralize 1 gram of the wax or waxy material.

The standard practice is to determine the acid value by warming 4 to 5 g of the wax with 50 ml of carefully neutralized alcohol in a 250 ml Erlenmeyer flask. A few drops of phenolphthalein are added and the titration made with vigorous shaking against a solution of approximately 0.1 N alcoholic KOH until a semi-pink color appears. A blank should be run at the same time and the titration if any deducted from that on the sample.

$$\text{Acid value} = \frac{v_w \times 56.104}{w}$$

$$\text{Free waxy acid } \% = \frac{\text{acid val.} \times M}{561.04}$$

Where M = molecular weight (m.wt.) of waxy acid

As the higher molecular weight waxy constituents are not particularly soluble in alcohol, it may be necessary with some waxes to resort to one of the following solvents: (a) equal parts of methanol and toluene, (b) 1 part of ethanol and 2 parts of light petroleum spirit (boiling point about 80°); (c) amyl alcohol or isopropyl alcohol.

For some waxes, in determining the acid number it is preferable to attach a reflux condenser and freely boil the solution for not more than 2 minutes.

Ester Value. The ester value is the difference between the saponification value and the acid value and therefore shows the amount of alkali consumed in the saponification of the esters.

If the wax is free from glycerides and resins

$$\% \text{ Esters} = \frac{\text{ester value} \times M}{561.04}$$

where M = molecular weight of the ester.

If the esters are glycerides then

$$\% \text{ Glycerides} = \frac{\text{ester value} \times M}{561.04 \times 3}$$

Estimate of Esters: Taking M at 621 as an ordinary value for natural waxes, the percentage of ester is roughly 1.1 × ester value. For example, carnauba wax has an ester value of about 78, then 78 × 1.1 equals 85.8. The actual amount of esters in carnauba wax is about 81 per cent. The types of esters in carnauba wax would, however, have a mean molecular weight above 621.

Another example is candelilla wax. The wax from *P. pavonis* has an ester value of 41.5; 41.5 × 1.1 equals 45.65. The percentage of esters and lactones is about 41. The lactones are of lower molecular weight than the esters, and hence the difference. More resinous species however give very much higher ester values.

Taking 841 as the mean molecular weight of the run of glycerides the percentage of glycerides is roughly 0.5 × ester value. For example myrtle wax gives an ester value of 210; 210 × 0.5 equals 105 per cent. The actual amount of glycerides is 97 per cent. This would indicate that the principal triglyceride was of a lower than common molecular weight. The triglyceride of myrtle wax is principally myristin and this has an m. wt. of 723.

Unsaponifiable Matter. Under the term *unsaponifiable matter* is included all substances found in the waxes which are insoluble in water and do not combine with the potassium (or sodium) hydroxide to form soluble soaps. In a wax the unsaponifiable matter consists chiefly of one or more alcohols, either straight chain or cyclic (sterols), occurring originally in either a free or combined state and the hydrocarbons.

In determining the unsaponifiable matter the alcohol is distilled off from the saponified sample and the residue taken up in about 200 cc of water and placed in a 500 cc separator; ether (200 cc) is added, and the whole shaken gently with a swirling motion. If undue emulsion forms, a few drops of alcohol and/or brine should be added. Extract the aqueous layer twice with fresh ether. Unite the ether extracts, and wash once with water to remove traces of soap and then concentrate by heating in a tared flask in a steam-oven until the weight is constant.

Iodine Number. The *iodine absorption value* or iodine number is determined with a "carrier" for the iodine, in which case the solution may be iodine monochloride in glacial acetic acid (Wijs); iodine monobromide in glacial acetic acid (Hanus); or iodine-mercuric chloride in alcohol (Hübl). The other reagents required in the test are standard tenth-normal sodium thiosulfate, potassium iodide solution (10 per cent) and dry chloroform or carbon tetrachloride.

Wijs solution can be prepared by one of two methods, the first more rapid and the second less expensive in materials.

(1) Iodine trichloride (7.8 g) and iodine (8.5 g) are dissolved in warm glacial acetic acid (HA) and made up to 1000 cc with glacial HA in the cold; or

(2) Iodine (13 g) is dissolved in a liter of glacial HA and pure dry chlorine (Cl) gas is passed through the solution until its titration number to thiosulfate is exactly doubled:

$$I_2+Cl_2=2\,I\,Cl$$

Hanus solution is prepared by dissolving together 13 g of iodine and 8 g of bromine in a liter of glacial HA.

Hübl solution: (a) Iodine (25 g) is dissolved in 500 cc of 95 per cent ethanol; (b) Mercuric chloride (30 g) is dissolved in 500 cc of 95 per cent ethanol. The reagent is made up by taking an equal volume of (a) and (b) when needed.

For Wijs, Hübl, or Hanus solutions:

$$\%\ \text{Iodine absorption} = \frac{(v_b - v_w)}{w} \times 1.27$$

where w is the weight of wax, and v_b, v_w are the respective number of milliliters of thiosulfate solution (reckoned as tenth-normal) used in the blank and actual analysis.

In the determination of iodine number by the *Hübl method*, an amount of sample is weighed out which will absorb 0.3 to 0.4 gram of iodine; this is then placed in a clean dry flask and 10 cc of chloroform added. When the sample has completely dissolved, 25 to 30 cc of the mixed iodine solution is added, and the flask stoppered carefully. The gutter around the stopper is filled with potassium iodide solution to guard against loss of iodine. Shake flash gently and set aside for 3 hours or more in a dark closet. A blank is run in a similar dry flask using the same amounts of chloroform, iodine solution, and potassium iodide. Add 100 cc distilled water to each flask and 20 cc of potassium iodide solution. Titrate the excess of iodine at once by means of the standard thiosulfate solution.

Hydrocarbon Analysis. In the determination of hydrocarbons in a wax a separation from the alcohols in the mixture can be effected by two well-known methods. The method of Leys depends upon treating the mixture with a hot amyl-alcoholic solution of fuming hydrochloric acid (HCl) to dissolve the alcohols, whereas the hydrocarbons (HX) separate out as an insoluble mass. In the Lewkowitsch method the alcohols are converted to the corresponding acids by heating the sample with soda-lime or potassa-lime; cholesterol, if present, remains practically unchanged.

Leys saponifies 10 g of the substance with 25 ml of alcoholic KOH

(45 g of KOH in 1000 ml of absolute alcohol and 50 ml of benzene). Use is made of an apparatus which consists of a round flask with a stoppered mouth at the top left and a stopcock fixture protruding from the middle of flask at the right, which in effect is a combined saponification vessel and separatory funnel. When the saponification is completed, 50 ml of hot water are added and boiling continued under a reflux condenser for a few minutes. The soap solution is drawn off while hot, and the benzene solution is evaporated to dryness in a porcelain dish. The residue is then transferred with 100 ml of hot amyl alcohol to a beaker and an equal volume of fuming HCl added. This is then boiled over an asbestos plate; the alcohols dissolve, whereas the hydrocarbons are taken off and boiled out once more with a mixture of 25 ml amyl alcohol and 25 ml fuming HCl. After cooling, the cake of HX is taken off, rinsed with water, the acid solution is drawn off, and the amyl alcohol solution well washed. The amyl alcohol is finally distilled off, the residue is dissolved in benzene. After evaporation of the benzene, the residue is weighed. The alcohols may be further examined if so desired.

Determination of Alcohols. Since the wax alcohols can be converted into wax acids by means of soda lime in the following manner,

$$\underset{\textit{cetyl alcohol}}{C_{16}H_{33}\cdot OH} + NaOH = \underset{\textit{sodium palmitate}}{C_{16}H_{31}O_2Na} + 2H_2$$

it is possible to measure the amount of hydrogen involved, and on the basis of the volume of liberated gas to compute the amount of alcohol originally present. Lewkowitsch gives the yields of 1 g of cetyl, ceryl, and melissyl alcohols as 184.4, 116.9, and 101.9 ml respectively, at 760 mm pressure and 0° temperature. These figures are equivalent to 1.652, 1.047, and 0.913 per cent respectively. The apparatus involved and details of manipulation are fully described by Lewkowitsch[3]. The reader is also referred to modifications of the method therein described.

Acetyl Number. The various hydroxy compounds that occur in waxes form derivatives on heating with acetic anhydride, the acetyl radical replacing the hydrogen of the alcoholic hydroxyl groups. This serves as the basis of analytical methods for the quantitative determination of these compounds. The *acetyl number* indicates the milligrams of potassium hydroxide required for the saponification of the acetyl assimilated by one gram of the wax on acetylation. On saponifying with alcoholic potash the acetyl is hydrolyzed to acetic acid and combines with the alkali to form potassium acetate. The results are expressed in terms of milligrams of potassium hydroxide to conform with the general practice in fat analysis. Hydroxy acids probably occur in wax as the result of oxidation of unsaturated acids. Solid alcohols of the cyclic series (sterols) occur in a few waxes both in combination as esters and as free alcohols. The amount of *cholesterol* or *phytosterol* is generally small, often inappreciable, and is indicated approximately by the unsaponifiable matter which it characterizes. *Alcohols* of the ethane and other series, free or in combination, compose a considerable portion of waxes. With fats the acetyl number serves as a measure of the hydroxy acids present in the form of glycerides. Naturally free alcohols, if present in fats, increase the acetyl numbers. Lewkowitsch found that free fatty acids of the stearic series may also react in such a way as to increase the apparent acetyl numbers, and he therefore preferred to acetylate the original wax rather than to work with the mixed fatty acids as recommended by Benedikt and Ulzer.

The method of Lewkowitsch is essentially as follows: Boil 10 grams of the wax with twice its weight of acetic anhydride in a round bottomed flask under a reflux condenser for two hours; pour the resulting mixture into a large beaker containing 500 cc of hot water and boil for half an hour. Allow the mixture to separate into two layers, siphon off the water, and boil the oily layer with three successive portions of fresh water. All free acetic acid removed, the acetylated fat is carefully separated from water and further dried by filtering through anhydrous paper in a drying oven.

Weigh two grams of the acetylated wax and saponify with a measured volume of standard alcoholic potash as in the determination of the saponification number; evaporate nearly to dryness to expel the alcohol, dissolve the soap in water and add an amount of standard sulfuric acid exactly equivalent to the alkali used for saponification. Warm gently until the fatty acids separate as a layer at the top. Filter through wet paper, wash with boiling water until filtrate is no longer acid, and titrate the filtrate and washings with tenth-normal alkali, using phenolphthalein as an indicator. Deduct the amount of alkali required to neutralize any soluble fatty acids in the original substance and calculate the acetic acid found in terms of acetyl number as defined above.

$$\text{Acetyl number} = \frac{\text{ml } N/10 \text{ KOH used to neutralize HA} \times 5.61}{\text{wt. of acetylated product taken}}$$

Generally speaking in the examination of waxes the acetyl numbers show the proportional amounts of free alcohols, together with any hydroxy acids if present. The Benedikt and Ulzer method was determined by the difference between the acid and saponification numbers of the acetylated acids (acetyl ether number).

Holland describes a modification of the method in which the amount of hydroxy compounds can be directly calculated. The difference between the saponification number of the fat before and after acetylation is per se the acetyl number. The formula employed is

$$H = \frac{cm}{56104d}$$

where, H = amount, c = acetyl number, m = molecular weight, and d = Number of hydroxyls.

Acetyl Number on Original Product (Mass Method)

	Molecular Weight	Saponification Number	Theoretical Acetyl number
Hydroxy acids			
Ricinoleic, $C_{17}H_{32}OH\cdot COOH$	298.45	187.99	187.99
Dihydroxystearic, $C_{17}H_{33}(OH)_2\cdot COOH$	316.47	177.28	354.56
Free Alcohols			
Cholesterol, $C_{27}H_{45}OH$	386.64	——	145.11
Phytosterol, $C_{27}H_{45}OH$	386.64	——	145.11

Another method, a gravimetric process, measures the increase in weight of the fatty acids produced in acetylation. This employs the formula

$$H = \frac{im}{42.036d}$$

where H = amount, i = increase in weight on acetylating, and d = number of hydroxyls.

In the Benedikt and Ulzer and Lewkowitsch methods the formula is

$$H = \frac{c(m + 42.036d)}{56104d}$$

Acetyl Gravimetric Process on Original Product

	Molecular Weight	Mol. Wt. After Acetylating	Theoretical Increase in Wt. (per Gram)
Hydroxy acids			
Ricinoleic	298.45	340.49	0.14086
Dehydroxystearic	316.47	400.55	0.26568
Free Alcohols			
Cholesterol	386.64	428.68	0.10875
Phytosterol	386.64	428.68	0.10875

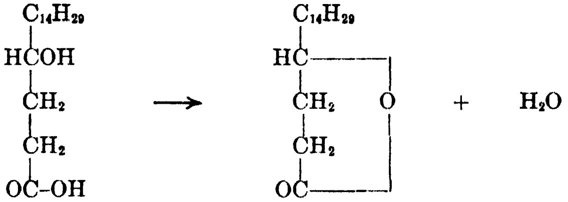
Acetyl Number on Acetylated Product (Benedikt *et al.*)

	Molecular Weight	Saponification Number	Theoretical Acetyl Number
Hydroxy Acids			
Ricinoleic	340.49	329.56	164.78
Dihydroxystearic	400.55	420.20	280.13
Free Alcohols			
Cholesterol	428.68	——	130.88
Phytosterol	428.68	——	130.88

Sterol Analysis. Mixtures of aliphatic alcohols and sterols when heated with concentrated sulfuric acid cause the alcohols to convert to alkyl sulfates, and the sterols to cyclic hydrocarbons. The alkyl sulfates can be isolated by means of the sodium salts, and the original alcohols are recovered therefrom by decomposition with boiling HCl. The method has not proved satisfactory for the wool wax alcohols.

Digitonin, a glucoside of digitalis leaves, is the reagent depended upon to precipitate cholesterols and many other sterols. If a hot solution of 1 g of digitonin in 100 ml of 90 per cent of ethanol is added to a solution of cholesterol in ethanol, a substance known as digitonin-colesteride is precipitated in a crystalline form. After standing an hour, it is filtered, washed, and dried at 110°. The crystals are easily soluble in pyridine, but insoluble in water and in most solvents. They are very slightly soluble in methanol and less so in hot ethanol. Phytosterol, stigmasterol, and many alcohols of other series form similar compounds, but the esters of the cholesterols do not interact with digitonin.

Lactone Number. A serious difficulty, which often confronts the chemist in the analysis of fatty acid mixtures, is the unstable character of the hydroxy-fatty acids. The latter are either (1) lactone-forming, or (2) non-lactone-forming. Lactone-forming hydroxy acids (more especially the γ acids) show a pronounced tendency to form inner anhydrides after being liberated. Thus γ-hydroxy stearic acid, after separation from its salts or esters, passes immediately into stearo-lactone:



Hydroxy-stearic acid *Stearo-lactone*

The non-lactone-forming hydroxy acids do not possess the property of yielding inner anhydrides. The hydroxyl group is therefore free to react with acetic anhydride during acetylation.

Hydroxy-stearic acid, $C_{17}H_{34}OH \cdot COOH$, of molecular weight 300.468, requires for saponification 1 molecular equivalent weight of KOH, 56.104. The milligrams of KOH necessary to neutralize and saponify 1 gram of hydroxy-stearic acid are then 56,104 divided by 300.468 = 186.72, the acid and saponification number.

However if the lactone exists with the hydroxy acid, the acid number will come way down. The saponification number however would be a trifle higher than if no lactone were present. For this reason an ether number will be shown that would otherwise be zero. This gives us an estimation of the amount of lactone.

	Acid Number	Saponification Number	Ether Number
Hydroxy-stearic	186.85	186.85	0
Hydroxy-stearic and stearo-lactone 1:1	96.31	192.62	96.31

The mean molecular weights of the lactone acids are calculated from the following formula

$$m = \frac{56{,}104 \pm 18.016(S-a)}{S}$$

where m = mean molecular weight, S = saponification of mixed fatty acids, a = acid number.

The lactone number is defined as the mg of KOH necessary to saponify the lactone in 1 g of acids. The lactone number is lower in the acetylated mixture.

	Acid Number	Sapn. Number	Ether Number	Acetyl Number	Lactone Number
Non-acetylated	96.31	192.62	96.31	——	96.31
Acetylated	89.83	269.50	179.67	89.83	89.83

Hübl Number. The Hübl number is the ratio of the saponification value of the neutral portion (wax esters, alcohol, and hydrocarbons) to the acid value. In general the ratio number is the ester value divided by the acid value for a natural wax, and amounts to 3.6 to 3.8 for genuine beeswax, for which it is commonly used to detect adulteration with East Indian waxes.

Reichert and Reichert-Meissl Number. The Reichert number is the number of milliliters (ml) of tenth-normal base required to titrate the acids obtained from 2.5 g of oil or wax by Reichert's distillation process. The Reichert-Meissl number is the same as the Reichert number except that 5 g of the oil or wax is used. The Reichert-Meissl number is not exactly double the Reichert number.

The Reichert-Meissl number of most oils, fats and waxes is less than one. The saturated acids that have been classed as "soluble," that is capric and lower carbon acids, are the only ones that will not decompose in the steam distillation. They are known as "volatile acids" whereas the higher acids, above lauric, are called "non-volatile." Lauric acid distills with steam but is slightly decomposed.

DETERMINATION OF PHYSICAL CONSTANTS

The more important of the physical constants to be determined for waxes are the following: (1) setting and melting point of the waxes and of their corresponding fatty or waxy acid mixtures; (2) specific gravity or density; (3) refractive index; and (4) viscosity of the melts.

Melting and Setting Point. The melting point of a wax and of its constituents is in general valuable not only in identifying and classifying the wax, but in establishing its purity.

The setting point, which is the temperature at which the molten wax begins to set for solidification, is substantially the same as the melting point for pure chemical compounds, but often wide apart from the melting point for mixtures of compounds.

Setting and melting points are determined by (a) closed capillary tube, (b) open capillary tube, (c) thermometer bulb method (drop point).

The melting point by method (a), or (b) is usually determined with a simple apparatus, consisting of a 100-ml beaker two-thirds full of a liquid of a high boiling point, a ring stand with clamps to hold a thermometer, a stirrer, e.g., a glass rod with a ring ¾ inch in diameter bent at right angles to the rod, a thermometer graduated by tenths of a degree, and several capillary tubes.

Drop Point Method. The dropping or drop point method requires that the thermometer with the wax applied to its bulb be inserted through a stopper into air or a gaseous zone, usually in a Pyrex test tube. The liquid in the beaker surrounding the test tube is selected from one of the following: water, sulfuric acid, olive oil, glycerin, phosphoric acid, or paraffin. However, jojoba oil if available makes the best heating medium.

Open Capillary Tube Method. The end of a piece of quill glass tubing is drawn out into a capillary. The substance is melted at a temperature slightly above the fusing point and then drawn up into the capillary tube, where it is allowed to solidify spontaneously. After an interval of not less than one hour and preferably twelve hours the tube, open at both ends, is attached by a cork or an elastic band to the stem of the thermometer in such a manner that the substance is at the same level as the bulb. The thermometer with its tube is then immersed in water, which is gradually heated at a rate not exceeding 0.5° per minute until fusion of the contents of the capillary takes place, when the temperature is recorded. It is desirable to immerse the beaker of water containing the thermometer in an outer vessel also filled with water, and to apply the source of heat to the latter.

Closed Capillary Tube Method. A modification of the above described method is the use of a capillary tube about 2 in long; the end is sealed off and the fragments of wax are placed in the capillary, or the capillary is flamed and the melted wax drawn in as the capillary cools. The thermometer with the capillary strapped to it is placed in the inner tube of a Fisher apparatus, which consists of an outer and inner glass tube, the latter with perforations, and corks. When heat is applied to the outer tube by a micro burner, the perforations on the inner tube set up convection currents in the liquid medium used, thereby producing a uniform temperature, necessary for exact determination of the melting point.

U Tube Melting Point. This determination is done in the same manner as above, except that a U tube capillary instead of a straight capillary is used. The melted wax is inserted in a U tube which has a long and short leg, and the wax then congealed. In the determination, at the critical moment the wax in the long leg will melt, and drop to the level of the rising wax in the short leg.

A.S.T.M. Methods. In the standard test method for the melting point of paraffin wax as adopted by the American Society for Testing Materials, the melting point is defined as the temperature at which melted paraffin wax, when allowed to cool under definite prescribed conditions, first shows a minimum rate of change. It also notes that the so-called "American melting point" is an arbitrary figure 3° F higher than the A.S.T.M. melting point. The A.S.T.M. determination is really one of a setting point. For details of the method and the construction of the melting point apparatus the reader is referred to A.S.T.M. designation D87-42, revised 1942. The apparatus consists of a wax container, air bath, water bath, stirrer in test tube, thermometer, and bath thermometer. "The melting point thermometer reading, estimated to 0.1° F, shall be observed and recorded every 15 seconds for at least 3 minutes after the temperature again begins to fall after remaining almost constant. The record of temperature readings shall then be inspected and the average of the first five readings that lie within a range of 0.2° F shall be considered as the uncorrected melting point. The temperature shall be corrected for error in the thermometer scale.

In the A.S.T.M. Method of Test for the Melting Point of *petrolatum*, the melting point is defined as the temperature at which petrolatum becomes sufficiently fluid to drop from the thermometer used in making the determination under definite described conditions. This is essentially the drop point method. In preparing the specimen the "thermometer bulb is chilled to 40° F, wiped dry, and while still cold thrust into the melted petrolatum so that approximately the lower half is submerged. It shall be withdrawn immediately, held vertically away from the heat until the surface dulls, and then placed for 5 minutes in a water bath having a temperature not over 60° F.

Dewar Flask Method. The specimen is put in a Dewar flask and heated on a water bath to some 5 degrees above its melting point. The bulb is taken from the water bath and constantly shaken and as soon as a skin begins to form, the thermometer is read every minute and the cooling point plotted. The knee of the curve shows the melting point.

The above method is essentially the freezing point (f.p.) method of Zhukov modified by Kissling.[2] In the Zhukov method 35 ml of paraffin are kept about 10° above its freezing point for 30 minutes in a 50 ml Dewar flask provided with a thermometer graduated in 0.1°, then allowed to cool, and the temperature read at minute intervals after the liquid becomes cloudy until it remains constant for several minutes. Kissling placed the flask in water, the water level being 1 cm above the paraffin. After heating for 30 minutes about 6° above the freezing point the paraffin is stirred with a warm thermometer, which touches the bottom of the flask. The freezing point is the temperature at which a deposit of solid paraffin appears at the bottom of the flask.

Maquenne Melting Point Block. An electrical microapparatus for the determination of melting points consists of a cylindrical aluminum block in the bottom of which is a spiral hole. This spiral cavity contains the heating element, which is protected by aluminum oxide. The bulb of a thermometer lies horizontally in a hole bored near the surface of the block. The whole block is surrounded by a bronze ring which projects 4 mm above the surface of the block. The substance being tested is placed on a cover glass resting on the bronze ring. The melting of the sample (about 0.1 mg) is observed by means of a lense, after which the used sample is removed by a wad of filter paper. The Fisher-Johns melting point apparatus employs a similar principle with modification. The samples are placed between cover glasses on an aluminum stage which is likewise electrically heated. A magnifier above the sample makes it possible to see the actual point at which melting takes place. The side armored thermometer is graduated from 20 to 300°.

Ubbelohde Drop Point. The Ubbelohde drop point apparatus consists of a porcelain scale thermometer (range 0° to 110° in 1/1° C) to which a cylindrical metal sleeve is attached. A metal case which screws on to the metal sleeve with a small opening which acts as a pressure equalizer, and a cylindrical glass cup opening at bottom 3 mm in diameter. Primarily the apparatus was designed for determining the melting point of greases, but it may also be used for soft waxes. The procedure is to fill the glass cup with the sample of wax and then fit it in the metal case that is in pressure contact with the thermometer bulb. When the wax melts it will always form a drop close to the size of the 3 mm aperture.

Softening Point. The softening point of a wax is the temperature at which the solid wax begins to soften. A wax will soften more readily when heated in contact with water than when perfectly dry. The softening point will also vary to some extent with the weight applied to the test specimen. Since in technical use waxed surfaces frequently come in contact with liquids under pressure it becomes necessary to recognize the temperature at which the wax will lose its firmness and perhaps its utility as well.

Ring-and-Ball Method. Although the ring-and-ball method (A.S.T.M. designation E28–42 T, revised 1942) is one which was designed as a test for asphalts, tars, pitches, and resins, it is of considerable value in determining the softening point of many types of waxes. The apparatus is equipped with one, two, or four rings to use with the same number of balls. An equipment with a single ring is shown in Figure 20.

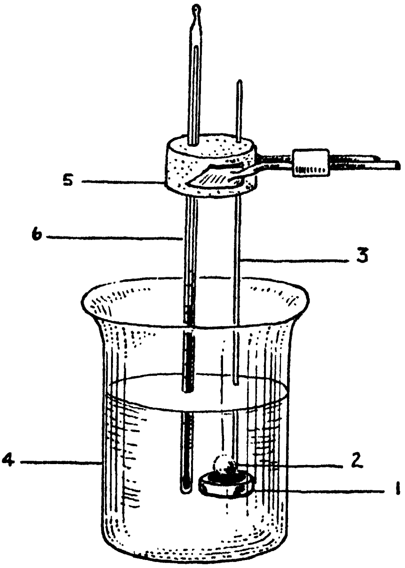


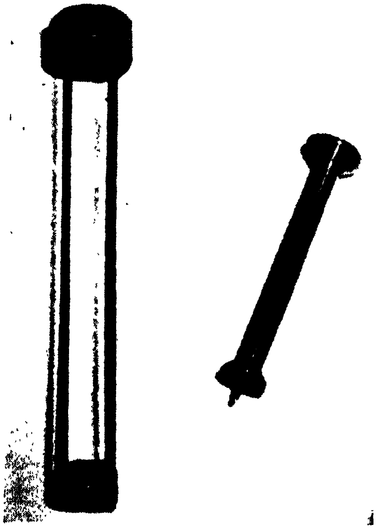
FIGURE 20. Assembly of ball and shouldered ring apparatus, showing single-shouldered ring. *Key:* (1) brass-shouldered ring; (2) steel ball, 9.53 mm in diameter, weighing 3.5 grams; (3) brass wire support for ring; (4) 600-ml low-form Griffin beaker; (5) rubber or cork stopper; (6) thermometer.

The procedure is to prepare carefully a sample of melted wax, and to pour it into the ring or rings which rest on a brass plate. After the wax has congealed the excess on the surface is cut off clean with a slightly heated spatula, the glass container is then filled with 9 cm of water, or with glycerol if the wax melts above 80°. The ball is centered on the upper surface of the sample. The ring containing the sample should be suspended in the water so that the lower surface of the filled ring is 2.5 cm above the bottom of the glass container. The thermometer is suspended so that the bottom of the bulb is level with the bottom of the ring. The ball is finally placed in the center of the upper surface of the material in the ring.

The heat is applied to the container in such a manner that the temperature of the bath is raised 5° each minute. The temperature reading indicated by the thermometer at the instant the sample touches the bottom of the container is taken as the softening point. The reader is referred to the "Tentative Method for Test for Softening Point, Ball and Shouldered Ring Apparatus," as published by the American Society for Testing Materials, for a more detailed description, and for designs of apparatus with multiple rings.

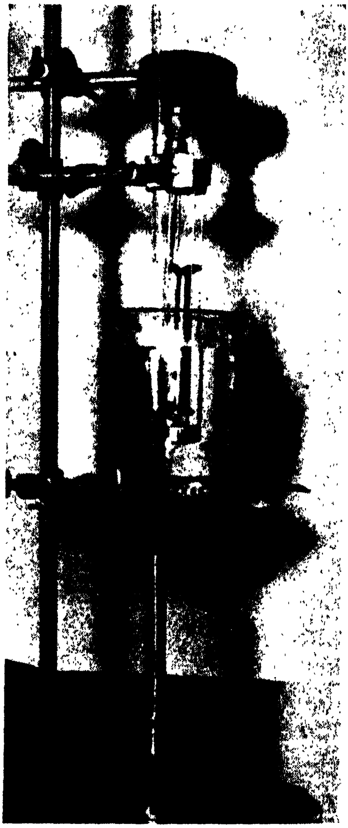
Ring-and-Plunger Method. Instead of the ring-and-ball method the softening point may be determined by a ring-and-plunger method. In the latter method the steel ball is replaced by a brass plunger, which is guided by a brass wire framework with rings at both ends.

The plunger has a shank 9.52 mm in diameter and 95 mm long. It is flanged to 20 mm at top end, and 17 mm at base end to which there is a pointed tip. The tip is 7.9 mm deep, and of large radius tapering from 3.2 mm to a dull point. Total weight of plunger is 75 grams. The frame is 178 mm high with support ring 31.7 o.d., 25.4 i.d., 12.7 mm deep, and has a lower ring 15.9 o.d., 12.7 i.d., 6.35 mm deep, for holding the wax specimen (see Figure 21).



Courtesy Crown Cork and Seal Co., Baltimore, Md.

Figure 21. Ring and plunger for softening point determinations. *left:* Frame with ring filled with wax. *right:* Plunger.



Courtesy Crown Cork and Seal Co., Baltimore, Md.

Figure 21a. Assembly of apparatus, showing position of frame and plunger for operation, electric stirrer, and thermometer.

The procedure in making the ring-and-plunger softening point determination is quite similar to that described for the ball-and-ring method. The apparatus assembly is shown in Figure 21a. When the wax specimen softens in the ring under heat the tip penetrates deeply and the base of the plunger touches the ring which holds the specimen. The temperature at that instant is noted as the softening point of the wax.

Solidification Point of Waxes. This determination is made under the following conditions:

(1) Temperature of water bath at the start of experiment is the same as that of the wax in the test tube.
(2) Mixer in water bath remains in motion throughout the period of test.
(3) The temperatures used at the start of the experiment should be 5° F above the drop point of the wax.
(4) When clouding occurs in the test tube, the temperature of the water bath sould be recorded. This will give the first indication of the solidification point.
(5) When clouding occurs in the test tube, the temperature of the wax should be recorded, and the stop-watch set in motion. The temperature should be taken after every half minute. The temperature, which has remained constant for a half minute, is the solidification point.

The temperature of the water bath when clouding of the wax first occurs, and the temperature of the wax which has remained constant for a half-minute, will not vary more than 0.5° F. The latter temperature should naturally be a trifle higher than the former. The great advantage of this method is that the clouding of the wax is uniform over the entire inner wall of the test tube.

Identification of Crystalline Substances. In the identification of pure organic substances derived from waxes determinations are made of setting, resolidification, and melting points. The setting or freezing point (s.p.) requires several grams of material and denotes the point at which the falling temperature hesitates or remains constant for a short period before it drops further again. The melting point (m.p.) and the resolidification point (r.p.) are made on a fraction of a milligram of substance fused in a convenient position on the side of a capillary tube 3 to 4 mm in diameter, sealed at one end. The tube is placed in the bath, the crystals brought into focus of a telescope and observations of melting point (m.p.) and resolidification point (r.p.) are recorded. The r.p. is the temperature at which the partly molten specimen in the capillary tube commences to solidify when the temperature is lowered very slowly. The values found for r.p. should be close to those found for s.p. Francis and Piper[1] used these methods in their determination of the melting points of the *n*-aliphatic acids and their esters. For example they found the following values:

Carbon Content of Acid	S. P.	R. P.	M. P.
14	53.65	53.9	54.4
16	62.60	62.4	62.9
18	69.39	69.2	69.6
22	79.70	79.6	79.95
24	83.90	83.8	84.15
26	87.41	87.2	87.7
34	98.00	97.8	98.2

Similar slight differences were found for the methyl esters, and the ethyl esters.

Specific Gravity. The specific gravity of a wax is usually determined at both room temperature (25°) and at 98 to 100°. If the wax melts above 90° the specific gravity is determined at the temperature of the melt or a few degrees higher. The specimen should be cooled for a number of hours at a temperature somewhat below the temperature at which the determination is made. This is especially true if measurements are made at 15° or below. The specimen is weighed in the air and in water. Let the volume of the solid be v, its density p; then its mass is $p \times v \times g$. When it is totally immersed in the liquid, the volume of the liquid which is displaced is also v; and its density is p, its weight $p \times v \times g$. The solid must not rest on the bottom of the liquid. The weight in air (strictly, in a vacuum is $p \times v \times g$; the difference in the two weighings, or the loss of weight is $p \times v \times g$. The ratio of these two quantities is p/p; therefore, if the density of the liquid is known, that of any solid denser than it, may be determined. If a solid has a density less than that of the liquid, which is the case with most waxes, it may be immersed in the liquid by hanging some very heavy solid below it, and then keeping this last solid immersed in the liquid during both weighings.

The specific gravity of a wax in the liquid state is best determined by means of a Westphal balance, employing a thermometer sinker. The balance must be placed upon a firm level table and carefully adjusted before using. In setting up the instrument the leveling screw must be directly beneath the arm that supports the beam. Place the latter in position and hang the sinker. The cylinder which holds the melted wax can be placed in a steam bath so as to maintain a 100° temperature for the wax. Lift the sinker, place the cylinder under the end of the beam and replace the sinker so that it hangs freely in the molten wax. The specific gravity is now found by placing weights on the beam until the balance is restored. The specific gravity (sp. gr.) is read directly from the positions of the weights on the beam. If the largest weight is 9, the second at 7, the third at 2, and the fourth at 3, the specific gravity of the wax is 0.9723 at the temperature recorded on the thermometer of the plummet. For a more accurate determination the same sinker can be used on an analytical balance.

Floating Wax Ball Method. The specific gravity of a wax can be determined in the following manner. Spherical balls of the wax are made by pouring the melted sample into a test tube of ethanol heated to 50°. A capillary tube may be used for introducing the drops of wax into the ethanol. These wax balls are then immersed in standard ethanol-water mixtures of known densities. It is necessary to determine the point at which the balls rise, and the point at which they sink. The arithmetical mean of the densities of the two ethanol mixtures is the specific gravity of the wax. The accuracy of this method however is open to severe criticism. It certainly is not accurate to more than the third decimal place.

Refractive Index. The index of refraction of a wax may be determined by (a) the Pulfrich refractometer, (b) the Abbe refractometer, (c) the Zeiss butyro refractometer, or (d) the Amagat-Jeans oleorefractometer.

Usually the refractive index is determined on the Abbe type of refractometer with water-jacketed prisms and provided with a special thermometer reading to 100°. It is customary to make the determination at 84° (183.2° F). The result is reported as $n\,\frac{84}{D}$; for example the refractive index of *dotriacontane*, $C_{32}H_{66}$, is $n\,\frac{84}{D}$ 1.4315.

Molecular Refractivity. The values of density and refractive index at the same temperature being known, molecular refractivities can be calculated according to the Lorentz and Lorenz formula,

$$Mr_L = \frac{n^2-1}{n^2+2} \times \frac{M}{d}$$

E.g., the molecular weight of dotriacontane was found to be 456 by the cryoscopic method, and the density at 84° ($d^{84°}$) to be 0.7687; then the molecular refractivity

$$(Mr_L) = \frac{(1.4315)^2-1}{(1.4315)^2+2} \times \frac{456}{0.7687} = 153.7$$

When theoretical values are calculated for the molecular refractivity of a hydrocarbon, 2.501 is taken for carbon, and 1.051 for hydrogen.

Crystal Spacings From X-Ray. The following description of procedure of determining crystal spacings (*A*, *B* or *C*) in Angstrom units (Å.U.) is taken from Francis and Piper.[1]

"To obtain x-ray photographs, flakes of the material are pressed in a thin layer onto a glass strip 5 mm × 1 cm, using the minimum pressure to cause adhesion. Heavy pressure or rubbing tends to distort the crystals, causing broad lines on the reflections. The plate is mounted vertically with its coated face in the axis of the rotation of the x-ray spectrometer, and parallel to a narrow beam of x-rays passing through the spectrometer slits. The beam is supplied by any suitable tune with a copper anticathode and is filtered by a thin nickel foil. The specimen is rocked to and fro by a cam mechanism, and the reflections are recorded on a strip of photographic plate or film placed perpendicularly to the x-ray beam and 5 cm from the rotation axis of the spectrometer. Reflections are recorded on both sides of the central beam, and the angle of rock is varied to suit the type of record required—about 10° for poor material, 20° for good. The spacings are calculated in the usual way for the Bragg law

$$n\lambda = 2d \sin \Theta$$

where n is any integer, d the spacing between the lattice planes parallel to the plane considered, and Θ the angle made by the incident ray with this plane.

"Exposure times vary from one hour to six hours or more with a Phillips type of tube running at 10 m.a."

Tables are given by the authors for the crystal spacings both *B* and *C* for the acids of even carbon content ranging from C_{14} to C_{38}, for C_{46}, and for those of odd carbon content with 17 to 29 carbon atoms. Values for the crystal spacings *A* are also given for their methyl and ethyl esters.

The spacings for CH_2 groups in the fatty acids vary in length according to the preparation of the specimen examined. If the specimen is a melt the value for the length of the bond between adjacent carbon atoms is referred to as the *C* value. For the straight chain fatty acids and alcohols the *C* value is 1.09×10^{-8} cm, equivalent to 1.09 Å.U. Where the specimen has been obtained as a result of very slow crystallization from a polar solvent such as ethanol, the crystals are distinctive; the value for CH_2 is 1.21 Å.U., and is known as the *B* value. If the specimen is the result of rapid crystallization, or contains impurities, the spacing measurement will be of the order 1.4 Å.U., which is referred to as the *A* value. Usually the spacing values are recorded as *C* or *B*, or both *C* and *B*. Crystals from a polar solvent are usually recrystallized from a non-polar solvent.

In making a mount it is sometimes advisable to first compress the powder to a pellet, when the specimen is recorded as "pressed on slide."

Physical Characteristics of Solid Waxes

The following characteristics are determined in grading waxes, more particularly the petroleum waxes, including the refined paraffins.

(1) The ***tensile strength***, or the force necessary to pull the wax apart.

(2) The *durometer hardness*, or the maximum force which may be applied to a small plunger in a wax cake without forcing it in further.

(3) The *consistency*, or the force necessary to push a plunger into the wax at a uniform rate. This is akin to viscosity.

(4) The *flexibility* of the wax as determined by a bending test which measures the force necessary to bend a plate of wax, and the angle through which it may be bent without cracking.

Tensile Strength. The tensile strength apparatus, or tensiometer, is illustrated in Figure 22. Two vertical lead-screws (1) drive a horizontal crosshead (2) at constant speed by means of a motor through a suitable reduction gear. To the crosshead is attached a Chatillon spring scale (3) to which in turn is attached a clamp for holding one end of the sample being tested (6). The sample is held by another clamp fixed to the base of the instrument. The applied load is indicated on the dial of the spring scale. The elongation is read to the nearest 1/100 inch on the vernier scale (4), and if more accurate readings are desired they may be made on the

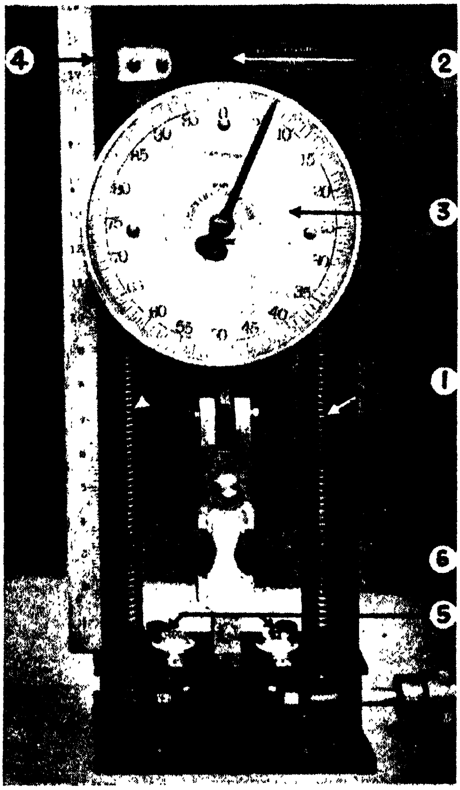


FIGURE 22. Tensile strength apparatus, or tensiometer. *Key:* (1) lead screws; (2) crosshead; (3) Chatillon spring scale; (4) vernier scale; (5) dials for precision reading; (6) specimen of wax.

Courtesy Atlantic Refining Co., Phila., Pa.

small dials (5) mounted on the instrument base. The entire apparatus is mounted in a constant temperature box with the heating and cooling systems necessary to give reasonably constant temperatures.

The mold used for the preparation of the sample is the standard A.S.T.M. asphalt ductility mold slightly modified by removing the sharp corners from the inside shoulders. This mold, as used for waxes, is shown with a sample in place in Figure 23 (left). A small box used to hold the mold is made by bending 1/64 inch sheet lead around a wooden block and folding the edges in such a manner as to make a tight one-piece container which is easily removable from the sample when the wax has solidified and cooled sufficiently to permit handling.

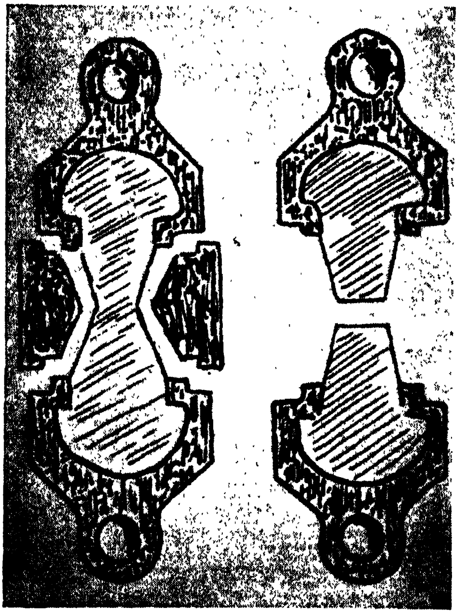


FIGURE 23. *left:* Mold used for tensile strength test, with sample in place. *right:* After testing wax of low ductility.

Procedure. In one of the small lead boxes is placed a flat piece of No. 24 B. & S. gage phosphor bronze to cover the bottom of the box to within 1/16 inch of the sides. Over this is placed a flat piece of 1/64 inch sheet lead of the same length and breadth. On this are assembled the four parts of the mold.

The box and mold are then heated to about 170 to 180° F, and the molten wax poured in to a depth of about ½ inch above the top surface of the mold. A small rectangle of sheet lead, followed by another of phosphor bronze of the same size, both preheated, are placed over the central part of the mold. The sample is allowed to cool until solid throughout.

The lead box is then stripped off; the excess wax cut away and the lead and phosphor bronze strips removed. Next, the side pieces of the mold are removed and the sample is placed in the constant temperature box and allowed to age overnight. To place the sample in the tensiometer, the crosshead is lowered until the end pieces of the mold fit the clamps easily. The pointer on the scale dial is then returned to zero position. The crosshead is raised until the pointer on the dial just begins to move, at which point the motor switch is again opened and a reading made on the elongation scale (4), after which the motor is again started and the crosshead raised until the sample breaks. The maximum pull attained is taken, correcting for original zero position, as the tensile strength. Figure 23 (right) shows a low ductility wax after the tensile strength test.

At least three determinations should be made for tensile strength, and if these values do not agree within 10 per cent, three more should be run. If, of six values, four or more of the highest values agree, an average may be taken of these; otherwise an average value of all determinations made should be used, unless some of the values are obviously faulty. Some of the most common faults, producing values which should not be included in final results are: sample twisted or bent, bubble or other flaw in or near test section, and cracks.

Durometer Hardness. The durometer is a small instrument fitted with a blunt pin connected through a spring to a pointer on a dial (Figure 24). It is graduated into arbitrary units known as "durometer units." Hardness is measured as resistance offered by the sample to the penetration of the blunt pin. Temperature is maintained in an air bath provided with an air-motor-driven fan for good circulation, and with electric heaters regulated by means of a rheostat and thermo-regulator.

Although the durometer is designed to be hand-held during the test, it was found that far more consistent results could be had by using a suitable mechanical holding and releasing device. For this purpose a cylindrical lead weight (1¼ in diameter × 4 in long, weight 1350 gm including shaft) is connected by a steel shaft to the knurled knob on the durometer. The steel shaft slides freely through a guide mounted on the wall of the constant temperature box, and the whole assembly may be raised or lowered by means of a heavy cord extending through the top of the box. A steel plate provided with leveling screws is furnished as a support for the sample.

Molds, of carefully machined brass, are used to obtain a sample cake of convenient size and shape—about 3 in square × ¾ in thick, with flat, parallel faces.

Procedure. The sample is melted and molded in the special mold. When solid, it is removed from the mold and placed in the constant temperature bath and maintained at the test temperature for at least one hour, assuming the sample to be at or near room temperature when placed in the box. At the end of this time the sample is placed under the durometer, which is held over and off the sample by the cord through the roof of the box. A small circular level is placed on the surface of the wax and by means of the leveling screws the sample is adjusted until the upper surface is level. The level is removed and the weighted durometer lowered by means of the cord until the full weight rests on the sample. Observations are made on the durometer every 5 seconds and are continued until the value falls off the same amount for each of three consecutive readings. The point at which the fall at constant rate begins is taken as the durometer hardness.

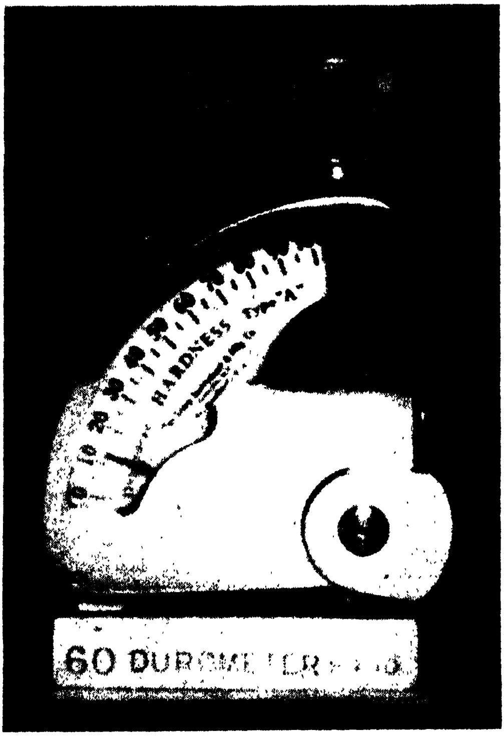
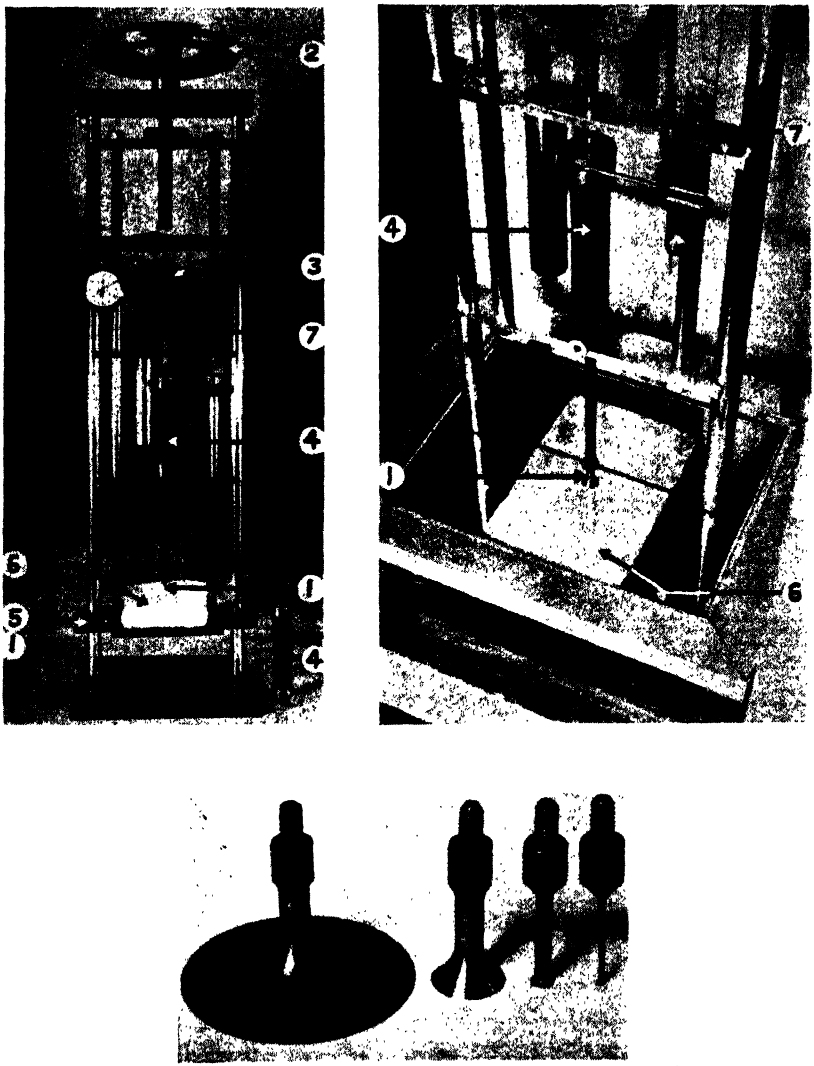


FIGURE 24. The durometer

Courtesy Shore Instrument Mfg. Co., N. Y.

Consistency. The Abraham consistometer is a vertical, manually operated mechanism (Figure 25) so designed that a push-rod carrying a plunger (1) may be driven downward at a definite and controlled speed by turning a hand wheel (2). Means are provided to measure the downward movement of the push-rod and plunger on a dial gage (3). Also, by means of one of two calibrated springs (4) and scale (7) the pressure required to produce or maintain the downward motion may be measured.

The springs provide two ranges, one from 0 to 1 kg, the other from 0 to 12 kg. Four plungers (1) numbered 1, 10, 100 and 1,000 are provided. These numbers refer to the approximate area of the face of the plunger in square



Courtesy Atlantic Refining Co., Phila., Pa.

Figure 25. *left:* The Abraham consistometer. *right:* Details of the consistometer. *above:* The four plungers of 1, 10, 100 and 1,000 square millimeter area, used for consistency test. *Key:* (1) plunger; (2) hand wheel; (3) dial gage; (4) calibrated springs; (5) adjustable platform; (6) specimen of wax; (7) scale.

millimeters. The consistometer is provided with a platform (5) adjustable for height, to hold the sample (6) in the proper position.

Figure 26 shows a convenient arrangement of the instrument. The entire apparatus is mounted in a special door (9) which may replace one of the doors of a constant temperature box. The upper section of this door is closed in back (10) and open to the front so that the controls and scales are accessible and visible, being in fact outside the cold box. The lower section, in which are the consistometer base (11) and the platform (5) carrying the sample, is open at the rear, thus making this compartment, in effect, a part of the constant temperature box itself, and this is aided by a detachable extension of a duct which circulates the air. The front of this compartment is closed by a small door (12) having hand holes to permit manipulation of samples without unnecessary loss of temperature. The partition (8) between the top and bottom compartments is of glass, through

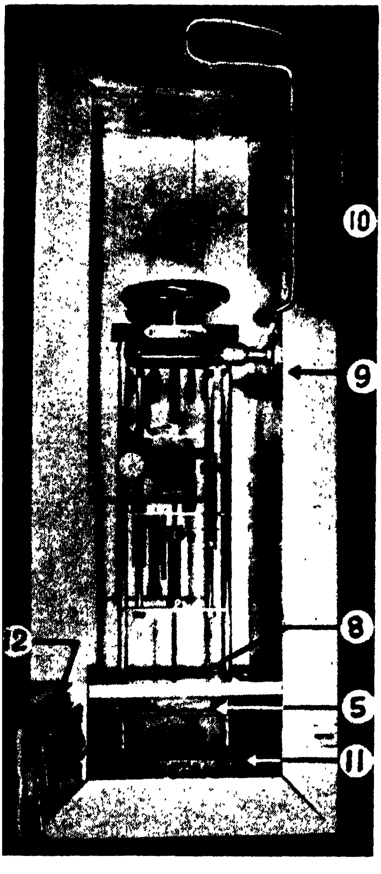


FIGURE 26. A convenient mounting for the consistometer. *Key:* (5) platform for wax specimen; (8) glass partition; (9) special door; (10) back wall; (11) consistometer base; (12) door with hand hole.

Courtesy Atlantic Refining Co., Phila., Pa.

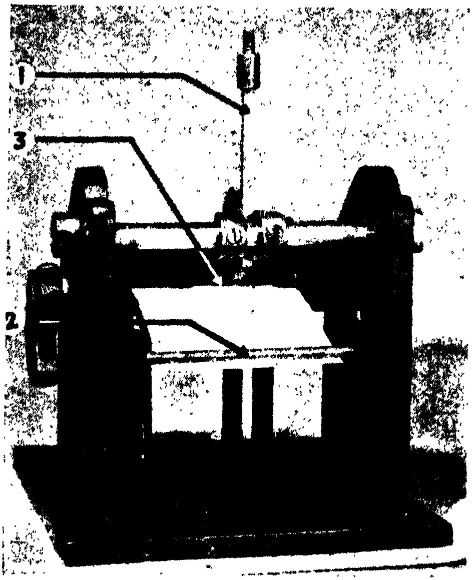
which extend the two supports for the apparatus and also the vertical push rod which carries the plunger.

Procedure. The wax to be tested is cut or molded to a size convenient for testing, preferably about 3½ in×4½ in×¾ in to 1 in thick. If molded, the sample is aged at least 18 hours at room temperature. It is then placed in the constant temperature box at the test temperature for at least three hours. The sample may then be placed on the adjustable platform of the consistometer and adjusted so that the upper surface of the wax is level and about ¼ in below the glass of the partition. A suitable plunger and spring are selected and placed in the apparatus. The plunger is then lowered until it just touches the surface of the wax. At this point the pointer on the gage indicating vertical travel is set to zero. A stop watch is started and hung on a hook provided for the purpose. By means of the hand wheel, the plunger is moved downward at such a rate that the pointer on the dial gage and the second hand on the watch move at the same speed. When moving at this rate, the plunger is being lowered at 1 cm per minute. Readings of the pressure required are made and recorded every 5/60 cm. These readings are plotted on semi-log graph paper. As the value at the 30/60 reading (½ cm penetration) has been found by experience to be the most reproducible, that value is taken as the consistency after application of corrections, if necessary. All readings are reported as kg per sq cm; *i.e.*, kg with No. 100 plunger. Results obtained with other plungers are converted to values corresponding to this plunger by suitable conversion factors.

Bending Test. The flexibility apparatus consists of a platform with a clamp (3) (see Figure 27) which holds the wax. A pair of arms carries a cross-rod (2) through which pressure is applied near the end of the wax sheet, causing it to bend over the rounded end of the sample platform. The arms are moved through suitable gears by pressure applied by means of the Abraham consistometer, to which the bending tester is connected by a rack (1), as shown in Figure 28.

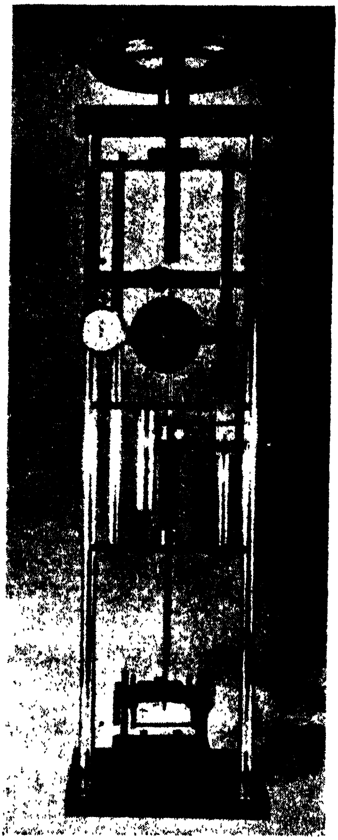
The consistometer is the same as used for consistency tests, except that the bending tester is substituted for the plunger and sample platform. The entire apparatus is mounted in a constant temperature air bath as described for consistometer tests, so that the sample and bending tester are inside the bath and are held at test temperature, while the controls and scales are outside.

Procedure. Sufficient sample to produce a sheet about 1.2 mm thick (35 gm for a 6 in×8½ in glycerin surface) is melted and poured on the surface of glycerin which has been heated 10 to 20° F above the melting point of the wax. The proper temperature for pouring may be easily ascertained by dropping a small chip or shaving of the wax on the cool glycerin; then heating slowly with constant stirring until the wax just melts. At this point, the heat source is removed and the melted wax poured onto the surface. Any bubbles present must be carefully removed. The wax and glycerin are allowed to cool to room temperature (or lower, if necessary) after which the wax sheet is removed and cut into pieces 2 in × 3¼ in. The sample, after being formed into a sheet, either before or after cutting into the small test sheets, is aged overnight at or near the test temperature. Following aging, the sample is held at test temperature for at least two hours and then tested.



Courtesy Atlantic Refining Co., Phila., Pa.

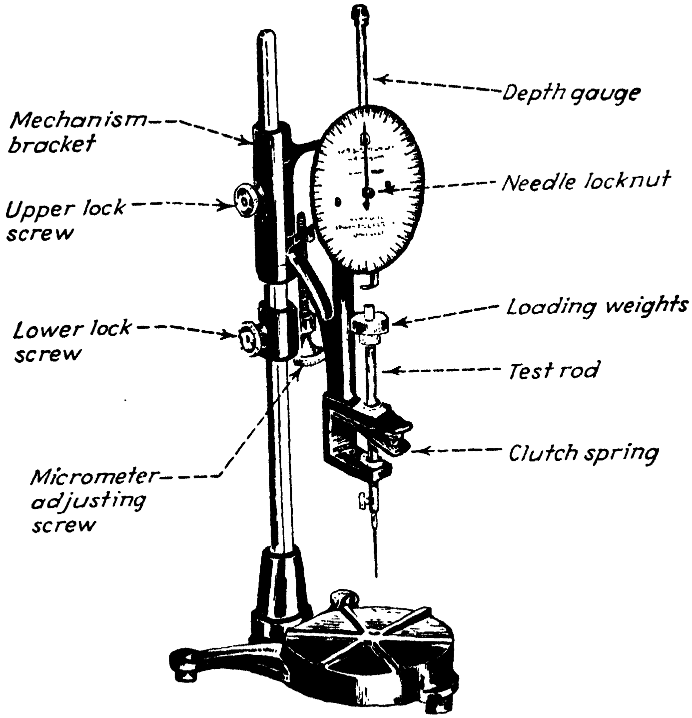
Figure 27. Wax sheet in flexibility apparatus. *Key:* (1) rack attached to consistometer; (2) cross-rod for pressure application; (3) clamp to hold wax sheet.



Courtesy Atlantic Ref. Co., Phila, Pa.

Figure 28. Flexibility apparatus connected to consistometer, ready for bending test.

The sample sheet is placed and clamped on the platform so that 2¼ in projects in front of the platform. The cross-rod (2) is then adjusted to



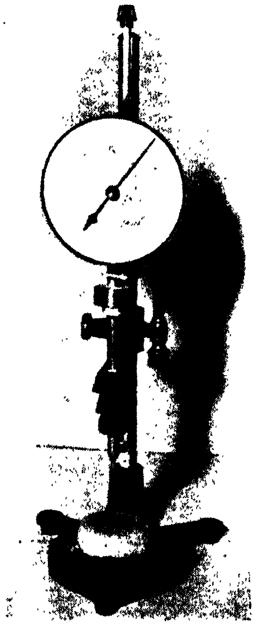


FIGURE 29. *above:* Diagram showing parts of the penetrometer. *right:* Photograph of precision penetrometer.

Courtesy Precision Scientific Co., Chicago, Ill.

just touch the upper surface of the sample. At this point the needle on the dial gage for penetration, as well as the scale showing applied pressure are set to zero. Pressure is then applied by means of the hand wheel so that the rack moves downward at a uniform rate of 1 cm per minute as shown by the dial gage. Readings of penetration and applied force are made at each 1/12 cm of downward movement. The reading at the point at which the sample breaks is also recorded. By means of suitable factors, from these results, the pressure applied to the sample and the degrees of bending are calculated. Each 1/60 cm downward movement of the rack is equivalent to 0.6° bend. Grams of force applied through the calibrated spring divided by 3.19 equals actual grams applied to sample. These results are reported as *degrees bend,* and *gm,* the latter value being the maximum force required during the test, calculated to grams on the sample.

Penetration Test. The penetration test is one that measures the depth to which a needle with a definite top load penetrates the wax sample. Where the conditions of test are not specifically mentioned, the load, time, and temperature are understood to be 100 gm, 5 sec, 25° (77° F), respectively, and the units of penetration to indicate millimeters. Details for the operation of the instrument (see Figure 29) are supplied by the manufacturers of the instrument.

The penetration test is particularly well adapted for microcrystalline waxes, and is more reliable than the durometer test in determining hardness. The penetrometer readings on highly crystalline materials such as spermaceti are not reliable, and the durometer must be resorted to in order to secure a proper measurement of their hardness.

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Chapter 9

Wax Technology—Uses in Industry

WAX IN ADHESIVES

The extensive use of wax in adhesives has come about within recent years. Waxes are now being used as adhesives in numerous ways. In some instances wax is a component of wet glues where it is used as a lubricating or flexing agent. An important direct use of wax during the war periods was in the preparation of an adhesive layer between two webs of paper to form the laminated moisture-proof wrapping material used to package cigarettes— as a replacement for metal foil. The various functions of wax in the adhesive art may be summed up as follows:

(1) As a laminating adhesive, with or without the aid of other material such as rubber, resin, etc.
(2) As a protective coating for wrapping which will by the aid of heat act as a "self-sealing" agent.
(3) As an ingredient of "hot melt" cements—useful in sticking dissimilar materials together.
(4) As an ingredient of the sticky surfacing agent for paper material, such as fly-paper.
(5) As a lubricator in glues; and as flexing agent in adhesives.
(6) As a combining agent with rubber and resin for making adhesive—waxed tape, and masking tape.
(7) As an ingredient of a rubber-wax adhesive which can be applied by heat to the end of a shot cartridge.

Waxes are generally considered as adjuncts to adhesives rather than adhesives, with the exception of *microcrystalline petroleum wax* of relatively high occluded oil content (10 per cent or more). This latter type of wax is sticky at ordinary temperatures. Waxes that are to be combined with resin, rubber, or glue to produce adhesives need not necessarily be of a tacky nature. Refined paraffin wax possesses both cohesive and adhesive strength when its melt is chilled, and finds an extensive use in bread wraps where the wax provides a means of sealing the ends.

Wax as a Laminating Adhesive. Microcrystalline waxes refined from petroleum tank bottoms or petrolatum, if not too highly refined, contain 7 to

15 per cent of occluded oil, are quite sticky and remain so at ordinary refrigerating temperatures. These waxes are black in color unless bleached. If partially bleached they are dark amber. Both the black and amber waxes find an extensive use in laminating. One of the well known amber waxes is "Petrowax," a product of the Gulf Refining Company. In the application of adhesive waxes to laminate paper materials it is customary to spread molten wax on one web, and moisture to the other, and then to independently heat each web at about the same temperature, and join the heated webs together. The purpose of moistening the uncoated web is to prevent it from becoming too dry, to increase its stretch, and to prevent warpage of the finished laminated sheet. In this method the heated webs with the adhesive layer interposed are subjected to pressure after being "wed," and then chilled to set the adhesive. Suitable laminating apparatus has been designed for the industry, and consists essentially of a series of steam-heated and chilled rolls about which the paper is trailed.

/ **Self-sealing Adhesives.** Paraffined wrappers are adequately self-sealing for the wrapping of cakes and bread. A paraffin wax of 133/135° F (A.M.P.) grade is commonly used for bread wraps. The addition of a hardening wax, such as candelilla, "I.G. Wax OP," and Asiatic paraffin of high melting point, to the paraffin wax has been proposed in order to increase the sealing strength of cake wraps. A "hot melt" coating of ethyl cellulose, colophony and wax suitably combined may be applied to glassine or other cellulosic sheet for the purpose of rendering the package both moisture-proof and seal-sealing. Wraps of this sort are used in packaging solid foods, including dehydrated material, for extensive shelf life.

Hot Melt Cements. The name "hot melt cement" is given in the trade to a solvent-free cement which requires heating to make it fluid, and cooling to make it congeal and stick. Hot melt cements are used to stick paper to metal, paper to plastic, metal to glass, etc. Adhesives of the hot melt type may vary in consistency from a sticky fly-paper adhesive to a fairly hard solid which will only become tacky when melted. Adhesives of the hot melt type do not always contain wax, but many of them do. Some of the resins used for the purpose are manila copal, processed congo copal, damar gum, methacrylate polymers, coumarone-indene, or other synthetics. Vegetable oils used with the resins may be boiled linseed, tung, peanut, castor, etc. Either refined paraffins or microcrystalline petroleum waxes are the most likely wax constituents, although there are many special formulae in which beeswax or a vegetable wax comprises the wax constituent. Natural rubber and butyl rubber are also constituents in some cements, where low viscosity of the hot melt is not an important requirement.

Sticky Fly-Paper. In the manufacture of sticky flypaper the paper web passes over a hot plate, or a series of hot rolls, to dry out latent moisture, and then through rolls which apply the adhesive on one side. By arranging the apparatus so that two of these coated webs face on the adhesive side, the paper can be rewound, cut to size, and the two webs pulled apart when ready for use in the household. Knoepfler[74] has given a composition for coating fly-paper which is made by heating together linseed oil 7½, castor oil 7½, beeswax 3½, and rosin 36 parts. Paraffin wax and ceresin wax are also used in some formulas for sticky fly-paper coating.

Wax as a Lubricator in Glues. Glues are improved in flexibility by the addition of a small amount of wax. The use of more than one per cent of a dry wax can destroy the adhesiveness of a wet glue. Hence the proportion of wax, such as ceresin, that can be advantageously added to a glue melt in water is about ½ to 100 parts of dry glue. In the manufacture of composition cork gaskets and gum wads the addition of a small amount of wax to the glue melt will facilitate the removal of the glue composited object from the metal mold which forms it. The wax can be used with animal glues, hide or casein, or with vegetable glues such as mazein and soya. The wax-containing glue is spread over the granulated cork, while the glue is hot, and after chilling the cork composition is packed in the mold; it is heated again to soften the glue and cause the adhesively coated particles to adhere to one another; this is followed by a chilling of the mold in order to finish the composition article and eject it from the mold. The presence of wax in the composition obviates the necessity of lubricating the interior of the molds prior to the packing operation. Industrially the whole process is made automatic and continuous by the use of equipment designed for the purpose. The term glue as used above is in the broad sense as it may have a polyhydric alcohol, a waterproofing agent, or other material added to it besides the wax.

Burgundy pitch, Venice turpentine, or low polymerized synthetic resins are sometimes used in combination with wax to mount metallic foils on felt, composition cork, etc. in the manufacture of liners for closures used in sealing glass bottles or jars, and open-mouth cans.

Adhesive-Waxed Tape. Adhesive-waxed tape is paper or foil coated with a wax composition which will become adhesive when subjected to heat and pressure. It differs from a masking tape which requires only pressure to apply it to another surface. Adhesive-wax tape may be also of such a nature that adhesiveness in its application to packaging is obtained through the use of a solvent to soften and activate the adhesion. These adhesively coated tapes, whether heat-sensitive or solvent-sensitive, have a wide use. The same principle applies to labels, sealing tape, papers for packaging, bottle-cap liner facings, initials or designs on fabrics, etc. In general, the heat-sensitive adhesives must not be too sensitive to climatic heats, otherwise the tape or foil would "block" in layers so that it could not be unwound from the spool.

Adhesive compositions suited to the coating of the tape or foil described above had been given by Kallander and Asnes[70] and have been used commercially. They employ wax, rubber, resins, and solvent, which must be mixed in a prescribed way. For example in preparing the K. and A. adhesive it is best to make up four different solutions:

(*a*) ester wax 5, paraffin wax 6, benzene 15 parts
(*b*) balata 10, crepe rubber 1, benzene 30 parts
(*c*) chlorinated rubber 1, benzene 5 parts
(*d*) vinyl acetate resin 2, benzene 3 parts

Solution (*b*) and (*c*) are added to (*a*) together with 30 parts of naphtha, after which (*d*) and 5 parts of alcohol are added. The compounding is carried out in a jacketed kettle, kept at a temperature of about 105° F. This type of adhesive permits considerable variation in the proportions of ingredients according to the type of adhesive tape required.

Masking Tape. A pressure-sensitive composition suitable for use on masking tape, tabs, posters and similar articles, can be prepared from rubber, resins, microcrystalline petroleum wax, and mineral oil, or similar combinations in which a wax is an ingredient. It is desirable to prepare a masking tape which can be attached to any surface by merely pressing the tape to the surface, and from which it can be readily removed without fowling or marring same. Abrams and Forcey[1] have given the following recipe for a peelable composition: rubber 30, coumarone-indene resin (m. 40°) 24, coumarone-indene resin (m. 10°) 28, microcrystalline petroleum wax (m. 155°) 15, white mineral oil 2, and hydroquinone 1 parts. The coumarone, (paracoumarone-resin) acts as the adhesive agent, the rubber as a cohesive agent, the wax as a modifier, and the hydroquinone as an antioxidant.

According to Abrams and Forcey[1] a composition suitable for application to a paper base for use as removable adhesive units, tabs or tape, may be made from: rubber 15, Vistanex 15, microcrystalline petroleum wax 19, methyl abietate 25, ester gum 25, and hydroquinone 1 part by weight. Glycerin may be added to the composition to facilitate clean peeling. The composition is applied to the base sheet by means of a heated doctor roll or blade and in a thin layer. The finished tab or tape may be applied to leather, textiles, paper, cardboard, Bristolboard, or to sheet material made of resins, viscose, cellulose acetate, hydrated cellulose and any other types of films.

Showcard Transparencies. Showcards, boards, fabrics, etc., can be furnished with a transparent foil or cellulose acetate by applying the latter to the entire surface with an adhesive composed of rubber, burgundy pitch and of crepe wool wax. The adhesive is prepared by adding a solution of 8 parts of crepe rubber dissolved in twice the quantity of petroleum ether to a preparation formed by melting together 8 parts of burgundy pitch and 4 parts of *wool wax*; 4 parts of petroleum ether are added after cooling. This adhesive is covered by a British patent.[9]

WAX IN THE BREWING INDUSTRY

Receptacles of large capacity in which malted liquors are customarily transported in the trade are barrels or kegs made of wood, or of metal. In order to prevent the adsorption of impurities from such a receptacle into the beer or ale it has been customary to provide a lining to the receptacle, and this lining is commonly referred to in the brewing trade as "pitch," irrespective of the exact nature of its composition. Brewer's pitch in a broad sense may then be defined as any pitch or pitch-like material suited for use in the brewing industry.

The cold water tanks, fermenting, and storage vats in breweries are also coated with wax, or wax compounds, which are fused by means of a blow torch applied to the interior of the vessel. Many of such vessels require relining after periods of use; the linings are durable but not permanent. This relining is done by trained artesans. The coating material used for lining or relining contains waxes like paraffin, ceresin, ozocerite, and montan. Some of the improved coating formulas contain microcrystalline petroleum wax, which is more liquid-proof than the refined paraffin wax.

The amount of wax consumed in lining beer cans exceeds 500,000 pounds per annum. The total amount of waxes used in the brewing industry is estimated as approaching 1,000,000 pounds per annum.

Colophony Pitch for Brewers. The simplest or cheapest form of brewer's pitch is a preparation consisting entirely of colophony. Colophony is the residue of rosin after the turpentine is distilled off. It is necessary to line wooden barrels or kegs in order to preserve the wood from decay, and to provide an extremely smooth cleansable surface for the inside of the keg to which impurities will not adhere. Colophony serves the purpose quite well. In the handling of receptacles in the trade the interior lining is exposed not only to physical damage, but biological, and it is essential and customary not only to cleanse the returned "empties" to remove the sour dregs, but frequently to repitch them so as to have a container without interior imperfections.

Colophony as a lining material has a mildly antiseptic property, and it is said not to injure the flavor of beer or ale. However, colophony has objectionable features, one of which is its susceptibility to minute fractures. It also is not entirely inert to water and alcohol, in consequence whereof the pitch coating has a tendency to disintegrate and become troublesome. The temperature of pitching must also be limited; if a colophony pitch is heated above 200° the beer will develop a disagreeable taste. Examples of satisfactory *rosin oil pitches are*: colophony 87, tasteless resin oil 8, and paraffin wax 5 parts; colophony 60, pine oil 30, resin oil 6, and paraffin wax 4 parts.

Bituminous Pitch for Brewers. The native bitumens have many of the desirable properties of colophony, but are more tenacious and durable, and are more inert to both water and alcohol. The bitumens are to a great extent brittle and must be plasticized to make them useful.

A brewer's pitch may comprise a hard bitumen, free from mineral matter, and a suitable tempering agent comprised of wax tailings combined with a petroleum pitch. Bitumens such as manjak (a hard bitumen found in the Islands of Barbadoes), gilsonite, grahamite, and wurtzilite are used.

In preparing brewer's pitch one or more of the hard bitumens are fused in a suitable vessel, and then a tempering agent such as wax tailings or wax from a still residuum is added in an amount sufficient to make the bitumen fluid enough to allow its application to the interior of the receptacle at a temperature between 150 and 200°. The requirements are that the resultant pitch must not soften under summer heat, must be adhesive, and must present a smooth and glossy surface, which can be readily cleansed. The addition of colophony and rosin oil to the bitumen-wax composition imparts antiseptic properties and improves the spraying qualities of the pitch. In pitching large tanks the brewer's pitch may be dissolved in a solvent naphtha and applied by brushing.

A recipe for an improved brewer's pitch of the bitumen type was given in the letters patent granted to Forrest.[46] This recipe calls for 35 to 50 per cent of hard native bitumen (such as Barbadoes manjak, 15 to 25 per cent of wax tailings (petroleum wax or still wax), and 35 to 40 per cent of colophony and rosin oil mixture (1 : 1). The whole combination melts to a proper consistency for application at a moderate temperature, is easily sprayed, and provides the smooth, hard, durable, elastic, clean, and cleansable coating which is required. It is also mildly antiseptic, lacking any taste or odor, and is insoluble in alcohol or water.

Satisfactory results for keg lining are obtainable with brewer's pitch made from any one of the following combinations: (1) petroleum wax and gilsonite; (2) crude montan wax, and a natural pitch; (3) Aruba bitumen, ceresin wax, and kidney rosin oil. Aruba bitumen, also known as "Vanadiset resin," is produced from Venezuelan crude oil at the Lago Refinery, located on the island of Aruba, N.W.I. Generically the resin is the same as pitch on the one hand and asphalt on the other. The grades range from 149 to 204° melting point. Kidney rosin oil is a rosin distillate and possesses an objectionable odor which the author finds can easily be eliminated by preheating before compounding. It is valuable as a tempering agent.

"Imported brewer's pitch" is the name given to a pitch that has been shipped in the past from Continental Europe to the United States, and was generally prepared from fully mature pine or other suitable forest tree by a process of heating the viscous exudation separated from its volatile constituent, until it became of suitable consistency and flash point. To this residue a certain proportion of rosin oil was added to give the pitch the necessary flexing property.

Evaluation of Brewer's Pitch. A first class pitch for beer barrels should be as odorless and tasteless as possible, supple, of good consistency, stable to heating, of a high softening point, of high ignition point, and of low evaporation capacity at high temperature. An acceptable pitch will have an ash content of 0.05 to 0.07 per cent, a gravity of about 1.0487 at 15.5°, a moisture content of less than 1 per cent, will be free from fatty and mineral acids, and contain less than 0.5 per cent of total impurities.

Stability on heating is determined by heating the pitch for 30 hours at 193° (380° F), and then measuring the viscosity, which should not exceed 2.50 Engler degrees.

The usual method of determining the flexibility or elasticity is to dip thin strips of smooth red beech wood ($1\frac{1}{4} \times 8\frac{1}{2} \times \frac{1}{16}$ inches) into the melted pitch at 205° (400° F); the strip is withdrawn and the film coating permitted to cool slowly to about 10° (15° F). The strip when bent and broken should not crack or flake off, if the pitch is supple.

The softening or flow point is determined by the A.S.T.M. ring and ball method. An approximate melting point is obtained by the drop point method, or the A.S.T.M. cube method for tar pitches. The softening point should exceed 45° (113° F) and the drop point 55° (131° F), since the temperature of the water in the keg washer is sometimes over 40°. If the softening point of the pitch is too high, the pitch will not penetrate sufficiently into the base material and is apt to crack.

Pitching Metal Barrels. Metal barrels are extensively used for packaging malted liquors. The barrels are of steel, stainless steel, or more often of aluminum. The colophony pitches so successfully used to line wooden barrels and kegs do not hold up well for metal containers. A satisfactory coating material may be prepared from colophony, bitumen, and 30 to 40 per cent of brown microcrystalline petroleum wax (m. 68 to 71°). A pitch of this sort flows quite freely under heat, and can be applied at a somewhat lower temperature (105°) than the colophony. The brown colored microwax is used because it is cheaper than the yellow, and serves the purpose well. The wax pitches can also be used to advantage in lining large vessels of stainless steel. Plain steel barrels must be well coated with an asphaltic pitch, although they are seldom used. Stainless steel kegs are only pitched to add a favorable taste quality to the beer. At Monterrey, Mexico, pitch lined half barrels of steel are pasteurized by the Luis Sada process, in a tray type pasteurizer after racking. Marketing pasteurized beer in so large a container is unique.

Pitch for barrels should have a high melting point but a low viscosity. For example, a new half-barrel of wood construction may require 13 to 15 oz of an ordinary pitch, but may be as effectively pitched with only 4 oz when the pitch is of a wax composition of a low viscosity specification. Aluminum kegs require more flexible pitch than those of wood, or steel, since aluminum has a high coefficient of heat expansion. Compositions for pitching kegs must be very fluid when melted, and therefore tank coating compounds, which are fused in small portions on the side wall of a tank, are not suitable for pitching.

Equipment for Pitching. The equipment used in pitching barrels and kegs can be classified as automatic, semi-automatic, or hand equipment. Fully automatic equipment from Neubecker a. Main is in operation in at least two breweries in the United States. This European system uses what is known as a "depitching pitch," with excellent solvent properties and fluidity, for removing the old lining from the returned empty keg. The keg is then moved to the pitching rack where it receives the new protective coating of pitch, the keg being drained and automatically revolved while heated to distribute the pitch clinging to the side walls. In this system a gas burner is not used for burning out the old pitch. Hence "checking," leaks, blisters, and other defects are avoided when pitching solid oak or plywood barrels.

Other systems not as fully automatic are the Harnischfeege, and the Schlange. Systems known as the Essinger, and the Rauch are semi-automatic. In the Rauch system, for example, there is a preheater known as the Universal Preheater, which employs artificial or natural gas; a small flame is applied so that enough heat is available for the quick and thorough removal of the old pitch without having the flame touch the container. The keg while very hot is then placed on the pitching machine. Usually there are one or two nozzles, each handling a keg. The spray nozzle is umbrella shaped and has about eighteen perforations which spread the pitch rapidly in a continuous stream to every part of the container, the excess pitch running into the well. The only moving machine part is a small inlet-valve in each pitch kettle. There is an automatic control which times the operation in seconds. The air-spray pipe admits air through the pitch spray while the pitch is draining out, thus carrying off any smoke or vapor.

Wax Lining Cans. Cans for packaging aqueous liquids, other than those to be subjected to high temperature sterilization, may in some instances be lined to great advantage with wax. Such cans are made with a pouring spout or open mouth; the beer cans with a conical "crown-finish" top. This top permits, in the course of manufacture, the entrance of a jet nozzle of a waxing machine by which means melted wax may be jetted into the can. The end having already been affixed to the can body, the wax at about 25 to 30° F above its melting point is jetted into the prewarmed container, by suitable automatic means. After waxing the can, the excess of wax is allowed to drain. The can is usually made of lacquered or enamelled thin plate which also permits a better attachment of the wax than plain metal.

A wax used for lining beer cans must be free from taste and odor, of a melting point appreciably higher than that of pasteurization, of low viscosity, and supple at refrigerating temperature. The wax used for the purpose contains a considerable proportion of microcrystalline petroleum wax in its blend. The cans are generally filled to a 12 fluid ounce level and "crowned" at the brewery.

According to Clayton, Johnson, and Sumner[25] wax can be deposited on the interior of a can by making the container the anode in an electrolytic deposition from an aqueous dispersion of wax. The dispersion is made to give "throwing power" in the electro-deposition. Subsequently the can is carefully heated so that the granulated wax deposited on the lining of the container is melted or fused, giving a uniform protective coating, About 30 to 50 amperes per sq ft in the initial current density and 3 to 8 amperes in the final current density are needed. The time of treatment is six seconds. The dispersions are made of sodium silicate, sodium aluminate, or other suitable electrolyte. The wax used is beeswax with paraffin, or ceresin, or a mixture containing a resin or a bitumen.

WAX CANDLES

Historical Development. The candle represents one of the most ancient and most useful forms of illumination. The candle is usually defined as a rod of fatty or waxy material through the center of which a fibrous wick extends. The excellence of a candle depends upon the nature of the wick and the combustible matter, and on the manner and extent to which these are apportioned. The prototype of the candle in the earliest days was most probably the *torch*, which must be regarded as a huge wick with the minimum amount of combustible matter; this proportion being altered until the ratio used at present, namely about one part wick to fifty parts of combustible material was reached.

The development of the candle to its present form is one covering a period of many centuries. It is believed that earliest man used a *torch* made of pine branches or slips saturated with resinous or fatty matter. Then came the *link* made of rope strands steeped in rosin, tar, or pitch—or still earlier in asphalt or bitumen. The link was followed by the *flambeau,* consisting of a core of hemp, soaked in rosin and coated with crude beeswax. Later the outer coat was made of bleached wax. The *dip,* which is the name for a tallow candle, is probably derived from the *rush light.* The latter had a wick of rush-pith, later of crude flax or cotton, and subsequently of twisted cotton yarn, coated with beeswax or tallow by repeated dippings; a counterpart is to be found in the *bougie* of continental Europe. Finally came the *molds,* which were candles introduced about the 15th century by the Sieur de Brez. In these molds the hard tallow, spermaceti, or at later date, paraffin wax, was cast around the wick of the mold. Varieties of molds are *rolled, poured* and *drawn candles.*

Paraffin wax was not introduced in candle making until 1854. The bulk of modern candles are made of paraffin wax, or of *stearine,* or mixtures of these. Most of the beeswax candles made are for church use. The candle-making materials are generally considered as candle grease, stearine (stearic acid), paraffin wax, ceresin wax, montan wax, spermaceti, and beeswax. The raw materials for the candle grease and stearine refining are bone grease, greases other than bone, palm oil, animal tallows, vegetable tallows, fish oils and fish stearin, and hardened fats and oils. The candle grease suitably mixed with paraffin wax is known as *candle mass.* In the manufacture of paraffin candles as small an amount as 2 per cent of *stearic acid* will stiffen the candle, but a larger quantity of *hydroxystearic acid* is to be preferred.

The plaited and pickled wick was first introduced in France in 1825. The early wicks, which were neither plaited nor pickled, did not bend over to the outer oxidizing region of the flame and consequently were not completely consumed; they required frequent snuffing to remove the char. Molding machines of a continuous wicking type were introduced in England in 1834. In modern machines 500 candles or more can be produced with one charge of the machine, and the output is two to three charges per hour per machine, in molded candles. In the United States the use of wax in the candle industry has grown to enormous proportion.

Dip Candles. The manufacture of *tallow dips,* which replaced the earlier rush lights, was conducted by alternate dipping and cooling of flax inkle in tallow, and was for centuries a household industry. In Paris during the 13th century a guild of travelling candle-makers went from house to house making candles. Tallow dips are still made to-day by numerous dippings of a plaited pickled cotton wick. Each dipping adds about an eighth inch to the diameter of the candle. Tallow dips are used by plumbers as a flux. Beeswax composition candles are made by dipping. Spermaceti candles came into use in the latter half of the 18th century. Spermaceti is used with some beeswax added to prevent brittleness in making the candle. For the standard sperm candle used in making laboratory measurements of candle power, not less than 3 or more than 4½ per cent of beeswax is permitted. The test air-bleached beeswax of about 144° F melting point must be used.

Tapers are made by drawing long strands of slightly twisted cotton yarn repeatedly through a bath of molten wax. The tapers are cut to length, the ends dipped in hot water and shaken. This process, called feathering, removes the wax from the one end, and thus allows a new taper to be lit easily without dripping wax. Tapers are used for lighting Christmas trees and festive cakes. Tapers are referred to by the chandler as *drawn candles*. *Lighting-wicks* are made in a similar way to tapers.

Formerly, the larger church candles were made by rolling a big cake of warm wax, kneaded until it was plastic, around a wick. Then, by means of a rolling pin the necessary smooth uniform finish was imparted to the candle. This process has now been superseded by that of pouring. However, poured candles are likewise rolled to secure the desired finish.

Rolled Candles. Beeswax and ceresin are waxes that do not lend themselves to molding. Beeswax candles such as thick, long altar candles cannot be well made by the dipping or molding processes, since beeswax contracts much on cooling and has a tendency to stick to the mold. To make the candle properly the melted wax must be poured over the wick until after successive coolings the required thickness is obtained. The poured candle is rolled between two boards, and then on a marble slab to give it the desired finish. Candles made from the microcrystalline petroleum waxes cannot be readily molded. Like beeswax, it can be formed into strong pliable sheets, that is, by expressing from a suitable die under pressure, as described by Rau.[101] The sheet material is then rolled into candles.

Highly ornamental candles are made of wax stained with suitable dyes and decorated with transfers or handwork. A handmade candle of distinction will combine color, form, and perfume, and will prove serviceable as well as ornamental. Some of these creations of modern times may follow the antique candles which belonged to Florence, Venice, Rome, or the Orient. Smooth shapes are hand rolled or hand twisted; *e.g.*, Antonio Ajello & Bros., candle craftsmen of New York, offer many varieties of distinctive candles in various color combinations with scents of honey suckle, orange blossom, etc., and in antique, French twist, tree, or character shapes. Candles of this sort are made of dripless and long-burning waxes, and have a standard corrugated base to fit the candle holder. A pine tree shaped candle for yuletide is made from *bayberry wax* which emits a pleasant odor.

Molded Candles. In the modern use of the term "mold" we refer to a candle which has been manufactured by a molding machine. The machine has several series of tubular molds in the center, wick spools below, and ejecting clamps above. The tubular molds are slightly tapered to facilitate ejection of the candles, and are fixed in a tank to which steam or water can be admitted. The lower ends are closed by the tip-molds which are carried each on a hollow piston rod. The piston rods are connected to a common bedplate. The upper or butt-ends open into a shallow trough. The clamps in the upper part of the machine are to hold the candles when ejected from the molds. Each mold has a spool of wick contained in a box under the machine. The molds are made of pure tin and the inner surfaces polished. The wick is threaded through the piston, through a perforation in the center of the tip-mold. The wick passes up through the mold and is held centrally by the candle last ejected into the clamp. The first step in the process of molding the candle is to pour the wax into the molds, which have been preheated to the proper temperature, leaving excess of wax in the trough. The candles are then cooled by filling the tank with cold water. The wicks are cut at the top and the clamps emptied. After the surplus wax in the trough has been scraped out, the bedplate is screwed up, and the candles ejected into the clamps.

As a paraffin candle tends to bend, it is necessary to stiffen it in one of several ways: by the addition of *stearine*, of *hydroxystearic acid*, or of a very high melting point *paraffin*. *Ceresin* is used for the same purpose. To give the paraffin candle oxygen-forming material as well as stiffness, 5 to 15 per cent of stearine may be added and it is then referred to as a "composition candle." In hot climates the stearine is considerably increased in the composition, or the candles may be made entirely of stearine.

Devotional Candles. Tallow dips are shipped from England to certain African tribes for their worship ceremonials. The Roman Catholic Church in its earliest period used beeswax exclusively for its altar candles. The Roman candles were long and tapering, whereas those of the Greek Catholic Church were short and stocky. To-day the Roman Catholic Church uses several types of candles of different composition. The two candles burning at the sides of the tabernacle on the altar, when mass is said, are liturgically specified to contain over 50 per cent of beeswax. They are usually white in color, in contrast to the brown color of the Greek Orthodox Church candles, which are made from the crudest beeswax. Devotional candles other than those used on the alter are molded from suitable candle material and invariably dyed yellow. If of long shape, they are best made from a composition of the following order:

paraffin wax 60, *stearic acid* 35, and *beeswax* 5 parts. The hydrogenated oils and fats serve as hardening agents for paraffin and are used chiefly for candles to be consumed in glasses, as in sanctuary lamps. A composition used for vigil-lights comprises *paraffin wax* 80 and *stearine* 20 parts. Vigil-lights are similar to the so-called night-lights. They are short, thick candles designed to burn six to ten hours, formerly made of *coconut stearine*, but now usually of a low-melting paraffin wax. They are molded without a wick, but are later supplied with a hard wax stiffened wick by insertion through a hole drilled in the wax cake. These lights give a very small flame. In Russia it was a common custom to sell the worshippers beeswax composition candles as a means of revenue to the church.

Candle Material. The petroleum paraffin wax used in candle making has a melting point of 52–53°, or 53–54°. Composite candles made of paraffin as the chief constituent melt at about 50°. The stearine used in making these candles will melt at 50–55°. The illuminating power is increased in proportion to the paraffin content; the oxygen in the stearine constitutes ballast and is of no significant value in illuminating power. Weight for weight, paraffin candles give about one and a half times as much light as stearine candles. Mixtures of *stearine* and *paraffin* always have a lower melting point than their individual components. In fact, equal parts of paraffin and stearine lower the melting point 6 to 9 degrees below that of the paraffin; but this mixture does not have a softening point as low as that of paraffin alone.

A cheap source of stearine was sought by the manufacturer of paraffin candles. On the other hand, the soap companies needed an outlet for red oil (oleic acid), which is a by-product in the manufacture of glycerin. In 1905 the Standard Oil Company[118] was granted a letters patent in Germany for a candle composition of paraffin and hydroxystearic acid, the latter dissolved to the extent of 40 per cent in stearic acid. *Hydroxystearic acid* is prepared by the candle maker in the following manner: The red oil is dissolved in a 60° Bé petroleum distillate and treated with cold concentrated sulfuric acid, while maintaining the temperature of the reaction at 40°. The sulfuric acid reacts with the oleic acid to form *stearolactone* (m. 51°) and to a much greater extent, *sulfostearic acid.* The reactants are then blown with live steam and hydroxystearic acid is formed from the *sulfostearic.* The steam-heated mass is allowed to stand, and the acid water is drawn off from below. The remaining mass is extracted with petroleum naphtha to dissolve the hydroxystearic acid, which separates out as a white mass on filtration, drying and pressing. About fifty per cent of the oleic acid will have been converted. The by-product, stearolactone, and the unchanged oleic acid are then distilled to yield raw material for use in making the next batch. *Hydroxystearic acid* is to be found in two forms, the one which melts at 77–85° and the other which melts at 81–85°. It is never used alone in making candles; always as a stiffening agent for paraffin candles. For the purpose of facilitating its solution in paraffin 3 parts of *hydroxystearic acid* are premixed with 1 part of the commercial *stearic acid.* Besides the process described above there are several other patented processes for converting oleic acid into hydroxystearic.

Candle material for colored candles is dyed in mass before molding, usually with alcohol-soluble colors. The stearine or composition wax is melted and the dye stirred in, the amount constituting about 0.01 per cent by weight of the candle mass. For red it is customary to use Sudan IV, phloxine, rose Bengal, or rhodamine; for yellow, chinoline yellow, or auramine; for green, caid green, or Victoria green; for blue, inulin, Victoria blue, or methyl violet. Monoazo dyes are suitable for coloring candles. Cheap, decorative candles are often dyed on the outside only by dipping the white paraffin candle in the dyed candle material.

Transparent candles for ornamental purposes may be made by adding to a paraffin melt about two per cent of β-naphthol, or by melting petroleum in the candle material. Martin[87] has given the following recipes: (1) paraffin wax 70, stearine 15, petrolatum 15, for a low melting transparent candle; and (2) paraffin wax 90, stearine 5, petrolatum 5, for a higher melting, less transparent candle. β-naphthol candles burn with a somewhat objectionable odor.

Candle Wick Specifications. The wick for a candle is generally a cotton yarn and is braided by machinery into an ordinary flat plait. It is supplied by the cotton spinner to the chandler who pickles it before use. Pickling is the treatment of the bleached plait with a solution of mineral salts, such as boric acid and niter, sal-ammoniac, or other suitable chemical to help fuse the ash of the wick when the candle is burned to prevent smoking. The pickling treatment is applied to hanks of material several days before the wick is to be used. The wick plaits are steeped in the chemical solution for 24 hours, then placed on a perforated shelf to drain, from which they are transferred to a centrifugal machine to dry them.

An important consideration in candle making is to adjust the size of the wick to the diameter of the candle and the fusibility of the candle material. The number of threads in each strand varies from 3 to 20. The size of the wick is indicated by the number of threads in each strand and the number of strands. Thus a 3–10 wick contains 30 threads in 3 strands of 10 threads each. The looseness of the plait is likewise determined by the same conditions and varies from 4½ to 18 per inch. A candle of very fusible and combustible material would have a looser plait than otherwise.

Shapes and Sizes of Candles. Stearine or composition candles are sold in many shapes and sizes, and are classified as to the number per pound, the length, and the diameter. In 12-ounce candles we have "short shape," "long shape" or "tube." A short shape, for example, might be 4½ inches long and $\frac{13}{16}$ inches in diameter with 12 candles to the pound; a long shape 9 inches long, ¾ inches in diameter, with 8 candles to the pound. A tube candle would be a long shape but smaller in diameter with 12 candles to the pound. There are other shapes and sizes in 14-ounce candles. There are also "self-fitting candles;" "cable toy" in assorted colors; "coach" which are 1⅛ or 1¼ inches in thickness; "night-lights" burning 8 to 10 hours; and "starlights." Candles are sold by the pound or box.

Molds in beeswax come in self-fitting or in plain ends. Tapering wax candles may be hollow or solid at the base. "Renaissance candles" are made in beeswax or stearine. Then there are the hand made patent-finish beeswax candles made in a number of lengths ranging from 9 to 22 inches. Easter or Paschal candles range from 32 to 64 inches in length and 1½ to 3½ inches in thickness. A 59 inch candle with 3½ inch diameter weighs 20 pounds.

Candles are also molded in prismatic cross-sections such as square, triangular, octagonal, etc. Spirally fluted candles must be made to rotate when ejected from the mold. Large church candles are often channeled by longitudinal shafts so that the melted matter will flow into the interior of the candle instead of guttering on the outside. Melted candle stock is also crutched previous to casting so as to secure more candles per given weight of candle stock. Such candles are consumed rapidly.

There is a popular demand for ornamental figurines in white and colors, with a central wick; *e.g.*, the "Tavern" novelty candles produced by the Socony-Vacuum Oil Co. They are made largely of paraffin wax in sectional molds.

Disinfectant Candles. Paraform candles are used for disinfecting the atmosphere in hospitals and in the home. They can be made from *stearic acid* 20, *paraffin wax* 40, and paraformaldehyde 20 parts. The stearic acid and paraffin are melted in a container with hot water or steam heat, and after thoroughly mixing and cooling to pouring consistency, the paraformaldehyde is stirred in rapidly as the wax is poured into water-cooled molds, to avoid loss by evaporation. Another composition which employs a 40 per cent solution of formaldehyde is as follows: paraformaldehyde 8, formaldehyde 5.5, *stearic acid* 16, and *paraffin wax* 16 parts.

Chinese Candles. Candles are made in China from a vegetable tallow obtained from the seeds of *Stillingia sebifera*, Willd. The seeds are about as large as hazel nuts, black in color, and are covered with a fairly hard layer of white tallow; the seed albumen also contains fat. The seeds are pounded in mortars, and exposed to steam for 15 minutes in cylindrical vessels, after which the mass is gently pressed. The congealed mass is warmed over hot embers and filtered through straw. Over 20,000 tons of this tallow are said to be produced in China each year. The tallow consists of *tripalmitin* and *oleopalmitin*, accompanied with small amounts of the glycerides of lauric, myristric, and stearic acids.

Solidified Alcohol. There is a demand for a canned fuel that can be easily handled and transported for the heating of small quantities of material. Commercial products of this nature have appeared on the market as "Solidified Spirit," "Solid Spirit," "Alcohol Cubes," "Travellers, Alcohol," "Smaragdin," etc. They are prepared by adding to commercial ethyl alcohol a solidifying ingredient, and when the mixture solidifies sufficiently, it is cut into cubes of one inch diameter, or other forms suitable for the market.

An early Belgian process was to add to the alcohol a sodium soap charged with several times its weight of sodium silicate, warming same and then allowing the mass to solidify. Soap and *paraffin wax* have also been used in the same way. Such preparations either decrease the calorific power of the alcohol substantially, and cause it to burn slowly; or they impair free burning and leave quantities of unconsumed residue. Cellulose nitrate[131] will increase the rate of combustion.

In one form of preparation the alcohol is solidified by the addition of 5 to 15 per cent of *vegetable wax*, *stearine* or *paraffin wax*, together with a sufficient amount of cellulose nitrate to impart the freedom of burning desired. In another preparation a synthetic tristearin, made from stearic acid and glycerin at a high temperature, is combined with a cellulose nitrate solution in such a proportion that the mass on cooling will separate out in a solid state. The temperature of mixing the tristearin and nitrocellulose should be maintained at 40°. One formula calls for tristearin 3, sodium sebacate 5, nitrocellulose in solution 1, and alcohol 91 parts.

Solidified alcohol produced from the latter cellulose nitrate formulation produces a flame with maximum heat, melts very slowly, leaves little residue, and obviates all danger of explosion. Cellulose acetate has also been used as the gelatinizing medium, and is said to keep the burning mass from excessive liquefaction. A small quantity of *stearic acid* adds greatly to the firmness of the product.

WAX IN COSMETICS

Historical. Cosmetics are substances of diverse origin skillfully compounded to impart beauty to the person. They have one or more of the following functions to perform: (*a*) to cleanse, (*b*) to allay skin troubles, (*c*) to cover up imperfections, and (*d*) to beautify. They have been in use since the days of the early Egyptians. For example, beautifully carved unguent vases in alabaster displayed in the British Museum date back to

3500 B.C. The earliest cosmetics were probably vegetable oils and tallows of a crude nature but fragrant. Those used later by the Romans, such as the solid unguents, were perfumed with almond, rose or quince. They were brought into Britain at the time of the Crusades. Cosmetics of all kinds were in great favor by the court of Louis XIII. The modern cosmetics that have a wax foundation include cleansing cream, greaseless cream, vanishing cream, skin cream, cold cream, unguent, lipstick, etc. They are simply refinements of many of the earliest cosmetics.

Wax Ingredients in Cosmetics. The waxy ingredients that enter into the making of cosmetics are *lanolin*, both hydrous and anhydrous, *white wax* (bleached beeswax), *cacao butter*, *stearic acid*, hard *microcrystalline petroleum wax*, as well as plain *paraffin*, *ozocerite*, *spermaceti* and waxy alcohols (*e.g.*, *cetyl alcohol*). In cleansing, vanishing, and greaseless creams, *stearic acid*, and alkaline reagents are included in the recipes. The alkaline reagents are principally borax, potassium carbonate, and ammonia. Triethanolamine is the alkaline reagent that is sometimes used with stearic acid.

Although only a fourth of the costmetics made in the United States contain wax or wax-like material, the volume of such cosmetics is estimated to exceed $25,000,000 in value per annum.

Emollients in Cosmetics. In recipes for cosmetics we usually find wax, an emollient, distilled water, an alkaline reagent, and a perfume. Cosmetics are prepared by emulsifying a wax in water by means of an emollient. The addition of perfume lends attractiveness to the cosmetic. The procedure in general is to melt the wax and the emollient together, and then slowly add to the hot melt the aqueous solution containing the alkaline ingredient, stirring to obtain a creamy and permanent emulsion. An emollient must be chosen that is compatible with both the wax ingredient, and the alkaline solution.

The emollients used in cosmetics are almond oil, white mineral oil, glycerin, castor oil, cholesterol, glyceryl monostearate, petrolatum, carbitol, and others. Any of these may be combined with the wax or waxy material and the alkaline fluid portion. The term "waxy material" implies the use of stearic acid. For example, let us consider the recipe for a greaseless cold cream of the following order: *stearic acid* 14, glycerin 12, potassium carbonate 4, water 8, borax 1 part, and perfume a.q.s. (a quantity sufficient). Without directions given with the recipe the logical procedure would be to melt the stearic acid in a kettle, with most of the water. The potassium carbonate and borax would be dissolved in hot water, and added to the stearic acid and water; after thoroughly stirring, the mixture would be beaten so as to saponify the stearic acid. Some time would elapse before adding glycerin, and perhaps the mixture would require re-heating, and then on cooling the perfume would be added.

Cold Cream. Cold cream may be regarded as a soft, oily, cooling cosmetic, consisting mainly of an oil, water, beeswax and a mild alkali. The alkali is one that assists in producing a water-in-oil emulsion, borax being selected for the purpose. It is of interest to note that cold cream originated with the French Pharmacopœia, the so-called *Codex Medicamentarious,* and that the French cold cream was virtually a rose-water ointment. English rose cold cream is of a similar order. It is prepared from liquid paraffin 61, white beeswax 18, rose water undiluted 20, and borax 1 part. Perfume and pink color, if desired, are added in small amounts. The perfume consists of French rose geranium 70, patchouli 20, and essence of synthetic musk 10 parts. The color consists of a trace of alkanin or amaranth.

The United States Pharmacopœia (U.S.P.) adopted the following recipe: *spermaceti* 125, *white wax* 120, expressed oil of almond 560, powdered sodium borate 5, stronger rose water 190, to make a total of 1000 parts. According to the directions of the U.S.P., the spermaceti and white wax are reduced to fine shavings and melted at a moderate heat. The expressed oil of almond is added, and heating continued until the mixture is uniform. Previously warmed rose water containing dissolved sodium borate is gradually added; the mix is stirred rapidly and continuously until it congeals and becomes of uniform consistency.

Commercial cold creams of today are made from a high grade bleached paraffin oil, which does not develop rancidity as does almond oil, and is less expensive to use. The paraffin oil used for the purpose was known as Russian white mineral oil. Other equivalents in white petrolatum oil or liquid paraffin are now being used. A commercial recipe for cold cream is as follows: *white beeswax* 150, white paraffin oil 600, sodium borate 9, water 240, and perfume 1 part. The white wax is melted in the paraffin oil by gentle heating. The borax is dissolved in the warmed water. The two fluids are brought to a uniform temperature not exceeding 60°. The aqueous solution is poured into the oily one in a continuous stream, stirring gently for a minute or two. Then while stirring, 1 part of oil of geranium and a little oil of rose are added. Sodium borate in cold cream greatly assists as a whitening agent.

In commercial production, when a mechanical filler is not available, a glass lined pot with a long spout may be used to pour the cream at about 40° to 42° into the jars. The vessel in which the waxes are melted should be glass lined, of stainless steel, aluminum, or other chemically resistant metal. Heating is best done on an electrically controlled hot-plate. Paddles for stirring should be made of wood. Artificial vanillin is not recommended as a perfuming agent since the cold cream is apt to turn pink and later brown during its shelf life.

Ceresin waxes have been used in making cold creams of a less oily nature. A recipe is as follows: white mineral oil 15, *white beeswax* 2, pure *ozocerite* 1, *white ceresin* 2, water 8.3, sodium borate 0.2, and perfume 0.06 parts. The waxes and oil are melted together; the temperature is lowered to 170° F and the sodium borate solution which has been previously heated to 170° F, is added slowly while stirring thoroughly. When the temperature drops to 150° F, perfume is added, and the stirring continued until the cold cream is ready to pour at 130° F.

Greaseless Cold Cream. There has been a market demand for a cold cream of a non-greasy type, one which will not leave an oily film on the skin, and which can be sold at a low price. These greaseless creams are prepared with *glyceryl monostearate*, or analogous material, which will permit making the cream with a higher water content than that found in any of the regular types of cold creams. A greaseless cream is more readily removed from the skin by means of plain water than the regular cold cream, but it is not to be recommended for a very dry skin.

A cream of the greaseless type may be prepared from *white petrolatum* 6, refined *paraffin wax* 5, *glycerol monostearate* 10, and white mineral oil 12 parts, with or without the addition of sodium borate to the water. The ingredients are melted together at 165° F and 50 parts of boiling water added while stirring with a forked blade. When the mixture becomes perfectly smooth and the temperature has been lowered to 130° F, a perfume such as rose is added. The greaseless cold cream can then be poured into the jars at a temperature of about 120° F. Some recipes call for a refined *diglycol stearate* instead of glyceryl monostearate. If sodium borate is used it is added to the boiling water to the extent of 1 to 2 per cent. Preference is given to the non-alkaline creams which are considered non-irritating to sensitive skins.

Cleansing Creams. Cleansing creams are closely related to cold creams, and are used for cleansing, or removing impacted greasy films from the skin. If they are facial creams their use is generally followed by some other facial treatment. Waxes are used in the preparation of cleansing creams, and usually a preponderance of oil, or more than in the regular cold cream.

Cleansing creams are prepared in different consistencies, such as "soft translucent," "medium translucent," "medium opaque," and "hard opaque." There are emulsifying and liquefying types of cleansing creams. In one of the emulsifying kinds, glycerin is used with water, *spermaceti* or *cetyl alcohol* is used as the wax, mineral oil as the emollient, and glycerin monostearate as the emulsifying agent. In another kind, stearic acid is melted in mineral oil, anhydrous lanolin added, and the hot oil mixture poured into a warm solution of triethanolamine in water, vigorously stirring until a good emulsion forms. Carbitol and quince seed mucilage are then added. Perfume is mixed separately with propylene glycol and stirred into the cream after it has cooled somewhat. The whole emulsion is then stirred at low speed until thoroughly cool. In the liquefying type, *ceresin wax* is used with white petrolatum and mineral oil and *spermaceti* may be added to make the cream firmer if so desired.

A cleansing cream containing magnesium hydroxide was patented by Walton.[126] It comprises beeswax, petrolatum, mineral oil, free magnesium hydroxide and water. Walton also proposed a skin cream comprising petrolatum, *cholesterol*, *ceresin wax*, magnesium hydroxide and water. A French letters patent granted to the Chas. H. Phillips Chemical Co.,[23] gives the following recipe for the skin cream: magnesium hydroxide. $Mg(OH)_2$ 2.4, *cholesterol* 2.7, petrolatum oil 30.3, *ceresin wax* 1, water 60.4, ethylene glycol 3 and perfume 0.2 part.

The value of microcrystalline waxes in cosmetic dermatology has been advanced by Erich Meyer,[90] particularly by the use of a micro-wax known in the trade as *Protowax*. Protowax is produced in the same manner as Petrolatum but is a cut made from slop-wax stock, and the finished sweated product has a melting point of 130° F. All of the oils included in the waxy particles having been removed, it would appear that the microcrystalline wax would tend to reabsorb oils, and this seems to be supported by the behavior of Protowax. The physical characteristics of Protowax differ somewhat from those of the higher melting micro-waxes. In appearance it might be described as a very stiff, white petroleum jelly. The use of a low melting micro-wax in place of paraffin, or to replace part of the ozocerite often used in cosmetic creams to prevent sweating, will result in homogeneous preparations, which retain their oil under conditions of use. The type of micro-wax described is not only of value in cleansing creams, but in formulating solid brilliantines, pomades, cream rouge, lipstick, etc.

Tissue Creams. Tissue creams fill a need for a cream that can be applied to the skin, especially the hands, to preserve it from prolonged contact with water, but which may be readily removed by soapy water. They are, generally speaking, modified cold creams, and of a non-alkaline or mild alkaline type. A non-alkaline tissue cream for example may be prepared from *spermaceti* 10, *lanolin* 20, *glycostearin* 46, olive oil 20, almond oil 30, and water 50 parts, with perfume added. A recipe for the mild alkaline type, which is less expensive to prepare, calls for white mineral oil 18, *white beeswax* 2, *ozocerite wax* 2, *spermaceti* 2, and *anhydrous lanolin* 2 parts. These ingredients are heated together in a double boiler, and 8½ parts of boiling water containing 2½ parts of sodium borate are added with continual stirring in one direction. The temperature is lowered before the addition of perfume and the cream then poured into jars. Another recipe calls for white petrolatum 4, white mineral oil 10, *lanolin anhydrous* 6, *diglycol stearate* 15, water 65 parts, and a little perfume.

Tissue creams of the above description, as well as other modified cold creams, become specialty creams when color and individual perfumes or medicaments are added. When the predominating constituents in tissue creams are animal or vegetable oils and waxes, the cosmetic is sometimes referred to as a nourishing cream. The efficacy of such creams in actually nourishing the skin is to be questioned. The ingredients in nourishing creams are of the following order: *lanolin,* cocoanut butter, *spermaceti, cetyl alcohol,* turtle oil, nut oil, and vegetable oil. A few of these specialty or nourishing creams will be referred to below.

Turtle oil cream is a nourishing cream which has turtle oil as one of its emollients. Turtle oil is an oil which is thick at 15° but fluid at 20°, and is slightly astringent; hence its value. The deodorized oil, mixed with an equivalent proportion of other nutritive oils, such as almond or olive oil, is compounded with lanolin and beeswax, as in the case of tissue creams, and colored with an oil-soluble yellow.

Avocado tissue cream is produced from lanolin absorption base, stearic acid, cetyl alcohol, beeswax, almond oil, avocado oil, perfume, sodium borate and distilled water. The sodium borate dissolved in the water is added to the melted wax and oil ingredients, and the cream scented with perfume just before packaging.

Specialty creams include such items as cucumber cream, colored with a little green dye and perfumed with cucumber oil; lemon cream colored with tartrazine yellow and perfumed with the essential oil of lemon; amond cream perfumed with benzaldehyde; menthol cream which contains 0.2 of one per cent of menthol; and peroxide cream. Peroxide cream is prepared by emulsifying *paraffin wax,* mineral oil, *lanolin,* a fatty acid ester, and hot water. Hydrogen peroxide and perfume are added when the temperature is lowered.

Cosmetic Cream Bases. In making specialty creams—creams which are highly colored, highly perfumed, or are to carry a medicament—it is desirable to start out with an emulsifiable base. Such a base may be prepared by adding concentrated potassium carbonate solution to melted stearic acid containing a little water, and then mixing the fused product with glycerol, wool fat and white beeswax after the complete evolution of carbon dioxide from the reaction of the carbonate and the acid. The base is made in the following approximate composition: *stearic acid* (free and combined) 35, potassium oxide (combined) 3, glycerol 51.5, *wool fat* 7, and *white beeswax* 2.5 parts.

Absorption base cream is the name given to a cosmetic cream base that is made from lanolin, lanolin derivatives and concentrates, or cholesterol compounds. An absorption base cream is prepared much in the same manner as cold cream. It is a soft cream, non-tacky and non-greasy to the touch, yet effective when used on dry skin. It is not unusual to combine with the lanolin or cholesterol compounds, some petrolatum and about five per cent of a fairly hard wax. The hard wax can be *ozocerite*, *beeswax*, *petroleum ceresin*, or the like. These absorption base creams have varied uses in compounding cosmetics; for example, they are excellent in preparing sun-protective preparations and require only the addition of the sun-screening agent. Formulas for cosmetics sometimes refer to absorption base cream as lanolin absorption base.

Protective Cream. Protective cream, also known as barrier cream, is used extensively by industrial workers to protect the arms and hands from grime, lacquer, solvents, etc. It can be readily washed off with water. There are several kinds of such creams on the market. An example is one made according to Formula 55 of the Atlas Powder Co., and which is prepared from: "Tween 61" 5, lanolin 25, castor oil 25, ceresin wax, m. 64° 5, and white petrolatum 40 parts. The directions are to melt together the lanolin, Tween 61, and castor oil; add the ceresin wax and when this is dissolved, the petrolatum. The product should be poured just before it begins to set. "Tween 61" is *polyoxyalkylene sorbitan monopalmitate*, which is a tan colored waxy solid with a titer of 35–39°, and a specific gravity of 1.06–1.07.

Creams protective against flash burns are on the other hand highly pigmented with titanium dioxide. Some protective creams of a water emulsion type are formulated using both "Span" and "Tween" emulsifiers, together with stearic acid, for example "Span 60," which is *sorbitan monostearate*, a waxy solid, and "Tween 60," similar to the Tween above described. These *non-ionic* emulsifiers find an extensive use in the preparation of drug and cosmetic emulsions.

Hair Straightener. Hair straightener is a pomade that is largely used for straightening negroid hair. It can be made according to the following formulation: white petrolatum 6, white beeswax 1, raisin seed oil 2 parts by weight. The petrolatum is melted in a double boiler and the other ingredients are then added. When the mixture begins to solidify a small amount of perfume is added. By increasing the amount of beeswax the product may be made stiff enough to cast into sticks if so desired.

Vanishing Cream. A vanishing cream is a cleansing cream which has the tendency to absorb and leave no greasy film when applied to the skin. Partially saponified *stearic acid* is the foundation for all such creams. In principle it is a stearic acid soap in which an excess of stearic acid is dispersed in water. Vanishing cream sometimes contains glycerin or *lanolin*, which acts as a softening agent and keeps the cream from drying out.

Some vanishing creams are opaque white, although a pearliness or silkiness is often desired and is brought about by the crystallization of the stearic acid, which takes many days to develop.

As an example, a vanishing cream can be prepared by melting stearic acid, 72 parts, in an enamelled double boiler, and adding to the melt slowly but with vigorous stirring a boiling solution of potassium carbonate 1, glycerin 25, and water 320 parts. *Triple pressed stearic acid* is the preferred acid. After completing the emulsification, the temperature is lowered to 130° F, the perfume added, and the whole stirred from time to time until cold. It is well to allow the cream to stand over night, stir the next day, and then pack into jars which are tightly covered immediately.

Lipstick. Lipstick is a rouge for the lips in the form of a stick or pencil. It is made up of four elements: wax, dye, pigment and emollient. The emollient used for the purpose should not only act as the softening agent but provide a mutual solvent for the other ingredients. The dye acts as a hue toner to the pigment. In the earliest lipsticks the wax was lanolin. The demand for firm lipstick pencils has led to the adoption of harder waxes, with or without lanolin. A selection is made of one or more of the following waxes: *beeswax, ceresin, carnauba, candelilla, spermaceti, cetyl alcohol, stearyl alcohol, hydrogenated vegetable oil, diglycol stearate,* and *white microcrystalline petroleum wax.*

The dye used to the greatest extent in lipstick manufacture is commonly referred to as "bromo acid." Bromo acid refers to mono-, di-, or tetra-, acid salts of fluorescein. For example, eosine which is the potassium salt of tetra-bromofluorescein is commonly used. The di-bromofluorescein imparts a different hue, an orange-yellowish stain. Phloxine, the potassium salt of dichloro-, or tetrachloro-bromofluorescein, and erythroseine, the sodium salt of tetraiodofluorescein are also used as dyes. The pigments are coal tar lakes or natural oxides, but usually lakes such as geranium red, rhodamine tolu-safranine, ponceaux, etc.

The emollients include almond oil which was in very early use, lanolin, lanolin absorption base, white petrolatum, liquid paraffin, *cacao butter,* and benzoinated lard. Stearo-ricinol, or a mixture of esters of polyhydric alcohols, and glyceryl mono-ricinoleate are now being extensively used.

Ordinary lipstick contains about 2 per cent of bromo acid, and about 10 per cent of colored lake, in sufficient white base to finish 100 per cent lipstick. The white base might consist of one part of *beeswax* and two parts of castor oil, modified by a little *white petrolatum* to soften it and make it spread more rapidly on the lips. Navarre[93] states that butyl stearate is a better bromo acid solvent than is castor oil, and that it is sometimes used to cut the thickness of castor oil films; its disadvantage is its tendency to bleed out. Lanolin is used as a blender, and is an emollient to the lips.

Beeswax is used in lipstick for its binding properties; in addition, it gives body, drag, and raises the melting point. *White beeswax*, is used in a proportion range of 5 to 40 per cent; too much of the wax will produce an undesirable granular lipstick. *Carnauba* and *candelilla waxes* give luster. *Lanolin* and *lanolin absorption base* possess emollient properties, and by acting as a binding agent for other constituents tend to minimize sweating and cracking of the stick, and give it a certain degree of plasticity. White mineral oil gives the much desired gloss, and makes the stick spread more smoothly and with less tackiness. It has no solvent power for the bromo acid. Petrolatum has been used to the extent of 20 to 25 per cent, but Navarre[93] noted that it causes the stick to drag too much. In lipstick manufacture it is well to use waxes of a high melting point. The lipsticks on the market have a variable melting point ranging from 52 to somewhat above 70°, although the more popular brands range from 55 to 60°. *Cetyl alcohol*, according to Harry,[57] has an unctuous effect and should not be used to exceed 4 to 5 per cent. Preference is given to cetyl alcohol because of its nice feel to the lips, but the use of both cetyl alcohol and *spermaceti* is limited because of their friability. Pure *stearyl alcohol* melts at 52°, and has been in use as a replacement for cetyl alcohol. It is a solvent for bromo acid. *Cacao butter* combines hardness with low melting point and excellent emollient properties, although it tends to bloom unless partially hydrogenated. Cacao butter has a smooth effect on lipstick but should be used only as a minor constituent. The so-called white absorption bases contain lanolin, refined lard, hydrogenated oils, etc. The lipstick material without the added color is known as the white foundation.

A typical formula for the white foundation would be lanolin absorption base 16, *beeswax* 15, *ceresin* 3, white *Micro Wax* 8, cacao butter 10, and liquid paraffin 5 parts. Another example would be cacao butter 6, *stearic acid* 3, *cetyl alcohol* 2, liquid paraffin 5, *spermaceti* 6, *beeswax* 20, *lanolin* 5, lard 20, and castor oil 5 parts. A simple formula has been given as *beeswax* 40, castor oil 30, and cacao butter 25 parts.

Wetting agents as well as perfumes find a use in lipstick manufacture. Perfumes in lipstick are coumarin, methyl coumarin, ethyl vanillin, and vanillin in conjunction with orange blossom, rose and jasmine bouquets.

The principle in the formulation of the mass for lipstick can be illustrated by a study of the white base foundation. For example, should we combine beeswax with castor oil we would secure good casts, but lack of luster, and the stick would leave a thick film. If we incorporated sesame oil and anhydrous lanolin in the mass, we would get a stick that would give a thinner and better adhering film, and so on. In formulating lipstick it is necessary that the texture be soft and creamy, suited for use in both hot and cold weather (it must neither drip nor crack) and further it must be in a condition to apply to the lips with a minimum amount of pressure. In lipsticks made solely with bromo acid as the coloring, the orange tint is changed on the lips to red. Black lipstick is prepared with a so-called "magic black," of which one per cent is added to the lipstick base. Although the lipstick pencil looks black, it rubs out to a deep red hue on application to the lip. "Personality lipstick," popular at one time, had a dye sensitive to slight changes in the pH value of the saliva.

In the manufacture of lipstick there are a number of stages, and these involve melting, milling, casting, removing, flowing, and filling the lipstick in holders. The customary procedure is to melt the fats and waxes and then keep the melt at a minimum temperature so that the pigment can be milled in. The dyestuff, bromo acid, is dissolved in the liquid ingredient, or emollient, after which this dye solution is added to the pigmented base, and the whole subjected to remilling. These milling operations are conducted by means of heat control. When the mass is freed from air and sufficiently cooled it is run into the sectional mold which has a series of cavities, all made of brass. The pattern consists of two halves which are capable of being clamped together for filling and taken apart after the sticks have been formed. The sectional mold is refrigerated and the sticks are removed when cool. A smooth finish is imparted to the sticks by passing them through a small flame. After this they are cased in a metal or other suitable holder.

In 1940 there were sixty or more brands of lipsticks on the market in the United States, with total sales estimated at eight-five million sticks having a wholesale value of $7,000,000 to $8,000,000 per annum. In 1945 the amount spent for lipstick was more than twice as much as sold in 1940.

Cream Rouge. The word "rouge" is given to a fine red powder prepared to impart color to the cheeks. Rouge in this powdered form does not contain wax. The term "rouge" is also given to colored powder, usually red oxide of iron, used as a polishing powder for glass, metal, gems, etc. When the rouge is made up into a pasty consistency for cosmetic use it is called cream rouge. There are several types of cream rouges; *e.g.*, they can be made up of a cold cream foundation, of a vanishing cream, or other foundation. Some preference is given to the vanishing cream type. Like lipstick they employ both pigment and dyestuff, as the coloring agents. The pigment is usually an organic lake, and the dye one of the fluorescein group. The white base foundation always contains wax, such as *beeswax*, *spermaceti*, *paraffin wax*, etc. For example, a cream rouge may be prepared from beeswax 4, paraffin wax 22, and liquid paraffin 74 parts, and color. The color—lake and dye—is added to the melted oil and waxes, and the whole mass is mixed and milled.

Eye Cosmetics. The principal cosmetics for use about the eyes are eyebrow pencils, mascara (a preparation for coloring the eyelashes), and eye shadow. All three preparations require wax in the foundation. Eyebrow pencils may be prepared from *beeswax*, hydrogenated cottonseed oil, cacao butter, castor oil, lanolin absorption base, and lampblack. If a brown stick is required the lampblack is replaced by umbers, burnt sienna, etc. When mascara is to impart luster as well as color to eyelashes, it is made as a greasy type, *e.g.*, a mixture of *beeswax*, *spermaceti*, *stearyl alcohol*, cacao butter, and petroleum jelly, combined with Oil Blue B.

Mascara in solid form is packaged by the manufacturer in small bars ($6 \times 1 \times \frac{1}{2}$ cm) with a brush which may be wetted for its application. It is also packaged in cream form (cream mascara) in metal tubes, labelled with color (black or brown), accompanied with a small brush for its use on eyelashes.

Eyeshadow may be prepared by combining *beeswax*, *spermaceti*, *lanolin*, cacao butter, petroleum jelly, and color. The color is either an organic lake or a natural earth pigment which must be considerably toned down with zinc oxide or titanium dioxide. The colors are blue, blue-gray, green, violet and brown, from which one or more are selected and milled into the base until a smooth product is obtained. Scintillating effects are obtained with bronze powder incorporated in the foundation.

Brushless Shaving Cream. Latherless or brushless shaving creams are to some extent replacing the lathering-type of cream on the market. The brushless creams contain besides stearic acid, one or more of the following waxes: anhydrous lanolin, spermaceti, cetyl alcohol, beeswax, Carbowax, and glycostearin. These creams may or may not employ a material of protein origin such as "Protinol," mazein, quince seed, sodium alginate, or the like. They also employ a saponifying agent in an amount which only partially saponifies the stearic acid. Emollients are added to soften and keep the creams from drying out in storage.

An example of a brushless shaving cream is given in the following recipe: *stearic acid* 200, *cetyl alcohol* 10, *lanolin anhydrous* 5, *beeswax* 10, sodium hydroxide 14, water 700, "Protinol-fine" 50, and preservative 2 parts. Another example is: *stearic acid* 165, *lanolin anhydrous* 39, white mineral oil 35, triethanolamine 10, borax 10, water 700, carbitol 15, propylene glycol, and preservative 0.5 parts. The general procedure for formulation of brushless creams is to melt the waxes and oil together, and then pour the melted material into a hot water solution containing the saponifying agent, such as the caustic alkali, amine, or mixture of both. The whole is mechanically paddle-stirred (to avoid foaming) until a smooth emulsion is obtained. Perfume and preservative are dissolved in the emollient, such as an alcoholic solution of "Protinol," and the solution added after the emulsion has properly cooled. Carbitol (ethanol-2-ethoxyethyoxy) and propylene glycol are also emollients.

Matumoto[88] reported Mollé shaving cream as consisting of: water 70.80, Na_2O 0.394, combined stearic acid 3.41, free *stearic acid* 14.20, *spermaceti* 3.75, and liquid paraffin 7.58 per cent.

Wax Alcohols as Cosmetic Ingredients. Cetyl, myristyl, palmityl and stearyl alcohols, because of their wax-like properties, have found important places in wax technology. *Lanette wax*, made in England, consists of a mixture of *myristyl*, *palmityl* and *stearyl alcohol*, and has been extensively used in formulating skin creams, ointments, etc. More recently *cetyl alcohol* has loomed in importance as an ingredient in ointment bases, superfatted cosmetics, lipstick, cream rouge, beard softener, shaving soaps and powders, and massage-, vanishing-, or tissue creams. *Cetyl alcohol* in its purest form (99.9 per cent pure) is prepared by the potassium hydroxide saponification of spermaceti. Cetyl alcohol is insoluble in water, but soluble in alcohol, chloroform, ether, the glycols, and aromatic hydrocarbons. It mixes with fats and oils, is tasteless, odorless, and non-irritating. On application to the skin it renders the surface velvety, rather than smooth and slippery. It is not affected by acid, alkali, light or air, and does not become rancid. Cetyl alcohol has been found helpful in creams for the treatment of eczema and pruritus. A commercial powder for such cases has been prepared from equal parts of boric acid and cetyl alcohol. According to Goodman and Suess,[54] cetyl alcohol forms water-absorbent emulsions, facilitates the inclusion of various medicaments, is readily incorporated in compounded ointments, and is claimed to aid in the passage of certain medicaments through the epidermis. Cetyl alcohol may be regarded as of general value in cosmetic dermatology.

WAX IN CRAYONS AND LEAD PENCILS

The word "crayon" as originally defined covered a drawing material, generally in the form of a pencil, but sometimes in powdered form, employed by the artist for drawings. The crayons were made in black, white and red colors; the black and red used for outline and shading, the white to heighten lights. Although originally prepared from vine black, native earth and other compact friable mineral substances, crayons are now for the most part artificially prepared mixtures of a base of prepared chalk, and pipe or china clay with Prussian blue, chrome yellow, vermilion, ochers, umbers, and other pigments cemented together by the introduction of some weak adhesive, usually gum tragacanth. Calcium gypsum, steatite, and compounds of magnesium, bismuth and lead are occasionally used as base. For example, a formula for making waxless crayons, which is given by Smith,[115] consists of a mixture of clay 75 lb, chalk 75 lb, starch 30 oz, alcohol 2 oz, soap 12 oz and water 4 gal. Hard wax crayons are made today in many striking colors with a base of stearic acid and about half as much paraffin.

Wax Crayons. The manufacture of crayons consists of preparing and molding the colored mass. The first step in the process is to mix the powdered color and steatite, or its equivalent together with a suitable amount of the stearic acid base in a closed rotating cylinder or ball mill, and the rotation is continued until the mixture is uniform in color.. The amount of color used is proportional to the wax and varies according to the hue, and its color strength. Between 8 and 25 pounds of color are used to each 100 pounds of base wax. Tints are made by using the pigment lithopone with the color, or in case of white the lithopone is used alone. The mixture from the ball mill is then made into a paste with a thin size, and kneaded to secure uniformity. The paste is then compressed in a horizontal brass or bronze cylinder having at one end a plate with an orifice slightly larger than the diameter to which the crayons are to be made. The paste is of such a consistency that a slight pressure will force it out of the orifice in front of the cylinder at a regular rate. The piston is put in position and the mass forced by uniform gentle pressure out of the narrow opening. The conveyor belt must move away at the same rate as the rod is ejected from the cylinder, so that a long stick of crayon mass rests upon it. This stick is cut up by a blunt knife into uniform lengths, which are dried upon boards with an absorbent paper. The rods shrink somewhat on drying, and when dry they are enclosed in casings similar to those of the ordinary lead pencil.

There is another process in which a thick paste is molded into blocks of the length of the crayons. These blocks are slowly dried at a uniform temperature and sawed by a fine saw into thin rods which are enclosed in a wooden case. The powder from the sawing is used in the next batch. The disadvantage of this method is that it is difficult to avoid cracks in drying the blocks, and a large number of the sawed rods break, even with the most careful treatment.

The colors used in crayon manufacture include lampblack, dip black, chrome yellow, primrose yellow, Indian red, Tuscan red, Prussian blue, raw umber, burnt umber, raw sienna, burnt sienna, American vermilion, French ocher, rose pink, Vandyke brown, rose lake, Venetian red, and chrome green (light, medium and dark). Colors are also composited to produce other hues; for example purple lake, para red, and lithopone are combined to give a purple of desired tone.

Pastels. Pastels are crayons that are made of coloring material diluted with a white base. They are made up into cylinders or pencils with the least amount of gum necessary to hold the particles of color together in the lightest possible manner, so that a touch of the pencil on the surface of the paper leaves an impression. Pastels for use by artists, are sold in a series of tones, usually six in number, the darkest pencil consisting of pure color; all the other pencils of the series are mixed with white to a greater degree as they ascend the scale towards the lightest. Thus the artist can select a certain number of tones ready to use at once. A pastel can be applied as a pencil by means of lines or short strokes, or it may be rubbed using the tip of the finger as a pad.

What is commonly known as a wax drawing pastel is somewhat different from the original artist's pastel crayon. The composition may consist of hard soap, wax and color. *Beeswax* and *spermaceti* are suitable wax materials. The melted waxes and the hard soap are mixed with the pigment and the mass ground until smooth in a heated mill. The finely ground pasty mass is then poured into water so as to secure binding of the colored wax material. In a white ground mass, white lead, zinc white, pearly white, or titanium oxide may be used to intensify the whiteness. Although gum tragacanth is a common agglutinant, glue and gum Senegal are also used. Oils, fats, and wax serve as agglutinants and produce gloss when so desired.

Ethyl cellulose and cellulose laurate have been proposed as wax adjuncts which will strengthen the crayon in the longitudinal direction by providing small stringy particles. These cellulose derivatives can be dissolved at an elevated temperature in *stearic acid*, or in mixtures of waxes: *ceresin, carnauba, beeswax, paraffin,* etc. The Eagle Pencil Co. holds a Canadian letters patent[39] for a pencil or crayon in which a filler and a pigment are united by a binder that includes water-soluble etherized cellulose and also small stringy particles of water-insoluble etherized cellulose, and a waxy substance composed of a mixture of stearic acid and a wax.

Marking Crayons. A crayon that is used exclusively for marking is made in a different manner from the artist's crayon and usually of much cheaper material. The manufacture of cheap wax crayons with paper wraps is not unlike that of the manufacture of candles, both in procedure and material. Marking crayons are made of different compositions in accordance with the material to which they are applied, *e.g.*, leather, cloth, metal, glass, etc. A French crayon made by Sciffini for ground marking is prepared from colophony 20, stearin 15, *yellow wax* 10, and chrome yellow 20 parts. A crayon for marking textile fabrics, as made by Beckers,[8] is formed of *stearic acid*, barium sulfate, and starch. A tailor's marking crayon requires a hard wax like *carnauba* blended with *paraffin wax*, and pure white talc. A glass marking crayon must be fairly soft and is made from paraffin, a little stearic acid and para red or other color. Weil[128] has proposed a luminous writing-stick composition made of *japan wax, ozocerite, paraffin* and petroleum jelly, together with a small proportion of luminescent sulfide.

Graphite Pencils. Graphite leads for pencils are made by mixing together graphite (including other carbons) and selected clays in proportions predetermined by experiment to produce what the pencil manufacturer calls *quality* and *degree.* The materials are mixed in water and ground in heavy mills; the quality is determined by the intensity of the grinding as much as it is by selection of material. The degree is regulated by the proportion of clay and graphite.

After grinding, the mass is transferred to a specially designed filter press and subjected to hydraulic pressure, to squeeze out surplus moisture and get a close texture. The compact mass is then inserted in power driven mechanical presses equipped with dies for the extrusion of the leads. The string-like plastic strip which exudes from the aperture of the die is laid on a board to dry. After drying, the leads are sealed in crucible boxes and fired in kilns to vitrefy the clay, at a cherry-red or higher heat.

When the leads are withdrawn from the crucible boxes they are impregnated with wax by immersing them in a wax bath at an elevated temperature. The wax enters and fills the interstices between the individual particles of graphite and clay, so that in effect the pencil lead is both plasticized and lubricated. The excess of wax on its surface is carefully wiped off or otherwise removed before the lead is placed in its cedar wood "coffin."

The waxes used for plasticizing and lubricating pencil leads are preferably waxes of high melting point, such as carnauba wax, but from so-called "close cuts" when petroleum waxes are used, *e.g.*, a petroleum ceresin of medium penetration value, an Asiatic paraffin of moderately high melting point, or the like. If the wax has a low softening point it may work out of the lead and loosen the glue bond between the lead and the wooden coffin, causing the pencil to split. This will happen despite the usual precaution taken to remove surface wax from the lead before it is glued and encased into the pencil.

The manufacture of leads for *colored pencils* is different, as the foundation consists of kaolin blended with suitable waxes and gums, which are ground together with the necessary color to obtain the hue desired. It is not a ceramic process. *Copying pencils* are made by blending graphite with aniline dye.

Wax-Soluble Colors. Ordinary dyestuffs and mineral colors are not soluble in waxes, nor are they soluble in oils. Therefore to color waxes it is necessary to use the so-called oil-soluble colors, for example Oil Yellow C Conc., Oil Brilliant Yellow, Oil Orange R Conc., and CCCC Oil Orange RG. One pound of the latter is sufficient to color 1000 pounds of a ceresin wax. In the blue range Oil-Soluble Blue S, an expensive brilliant blue of the alizarin series, and a cheap blue known as Oil-Soluble Dark Blue of the stearic acid type are available. Some of the recommended dyestuffs include Wax Yellow Extra, Wax Red G Conc., Wax Green G, Wax Violet, all of which may be dissolved directly in the molten wax.

Although the yellow and orange oil-soluble colors prove satisfactory, Proell contends that pink, violet, and other colors in the pastel shades do not, and he has now provided a new series of dyes which are substantially soluble, sun-proof, and heat-proof to temperatures of 250° F or more. Proell[100] incorporated into the *paraffin wax* metal organic dyes, such as colored metal oximes, particularly metal alkyl glyoximes. The alkyl radical dimethyl, diethyl and the like, and a heavy metal, nickel or cobalt are employed.

An example is given by Proell: "A paraffin wax-stearic acid mixture containing 25 per cent of *stearic acid* was heated to 250° F and 0.005 per cent of nickel dimethylglyoxime and 0.01 per cent of dimethylglyoxime added. The latter dissolved rapidly to form a yellow solution. This solution was filtered and chilled to just below the melting point of the wax without any deposition of the dye. Cakes of wax cast from this solution remained colorless until they had cooled further, when a pink color developed. The shell pink wax so prepared has an intensity of color equivalent to that produced with 0.02 per cent of Rhodamine B dye, but of a more violet tint.

"The necessity for heating the wax to about 250° F in order to secure a homogeneous solution may be avoided by dissolving nickel stearate in the paraffin wax base and adding a solution of dimethylglyoxime in melted paraffin to the mixture. Cobalt used in place of nickel produced a tan colored candle."

Proell further states that he had found that metallic salts of 8-hydroxyquinoline, for example, the bismuth and ferric salts, dissolve readily in paraffin wax compositions and give intense colors, the bismuth salt producing a lemon yellow color and the ferric salt a deep brown. Other metal organic compounds, such as metal salts of alpha-nitroso beta-naphthol, are further examples of compounds suitable for use as dyes in paraffin wax compositions. The cobalt derivative of the latter compound gives a dull orange color and the iron alpha-nitroso beta-naphthol a tan color to the wax.

WAXES FOR ELECTRICAL INSULATION

A large tonnage of waxes is used in the electrical industry, mainly for insulation. Paraffin is an excellent insulator at ordinary temperatures, but for purposes where the item coated becomes heated by an electrical current or otherwise, higher melting waxes or mixtures of wax with heat resisting material must be resorted to.

Insulating waxes are used for three principal purposes, (*a*) as a coating for wire, cable, or flat and irregular surfaces, (*b*) as an impregnant of another material, such as paper, wood, cloth, asbestos, etc. to increase its value as an insulator, or (*c*) as a sealing medium, that is for potting, end-sealing, and overall-dipping, *e.g.*, in the manufacture of capacitors. Different types of waxes are required for different purposes.

There is such a divergence in the products made or used by the electrical industry that the number of waxes and wax formulations employed run into the hundreds. There are, however, certain fundamental requirements for all of the waxes so used, and these are good ductility, low shrinkage, and good insulation value.

Wax for Coating Electric Wire. An insulating wax for coating electrical wires or other metal surfaces must be ductile, non conductive of electricity, and remain so under operating conditions. Paraffin has the unique property of showing an increase in its insulation value with temperature rise between 25 and 35°. In other words it has a negative temperature coefficient of electrical resistance between those temperatures before the coefficient again turns positive. Insulating waxes for coating are applied to stout electrical conductors such as cables, down to the finest sizes of wire as in variable and fixed capacitors of 5 down to 1 micro farads capacitance. Radio condensers require waxes of a more exacting specification than do the stout electrical conductors or the ordinary size wire. *E.g.*, the condenser in the small radio set in service becomes readily heated, therefore necessitating the use of a wax that will withstand at least 160° F of heat without softening or melting. Shellac wax, esparto and fiber waxes, when plasticized by an adequate amount of a softer wax also of high melting point, are suited for the purpose.

An insulating wax must be adhesive so that it will hold to the metal surface with tenacity, and it must be sufficiently ductile to permit the wires to be bent without cracking the wax coating, nor must the wax crack or pull away when chilled. The large coefficient of expansion of carnauba, and certain other hard waxes, makes the use of these waxes for insulation rather undesirable.

Wax for Coating Cables. An insulation wax for cables, *i.e.*, cable wax, differs somewhat from that for wires. *Cable wax* should have a melting point of 55° to 65°, should have no constituents that volatilize below 180°, and must not be sticky. It must be resistant to steam, weak alkalies, and acids, and inexpensive. Ozocerite wax conforms to these requirements except that it is too expensive. However, ozocerite has been used in conjunction with cheaper waxes, such as *japan*, *crude montan*, etc., or with stearin and rosin pitch. The high melting fully refined paraffins have excellent insulation value but lack the required tackiness to enable them to stick to metals. Diggs, *et al.*,[36] were probably the first to find *petrolatum wax* suitable for the purpose. The crude petrolatum obtained from a Salt Lake crude oil is not adhesive, but the crude may be dissolved in ethylene dichloride or naphtha and cooled to a temperature at which a high melting crystalline fraction precipitates. It contains somewhat over 15 per cent of occluded oil, melts at about 160° F, and shows a breakdown test in liquid state of O.K. at 25,000 volts. Today, microcrystalline petroleum waxes as well as the Diggs wax are widely used in the electrical industry.

Failures with Paraffins. The failure of underground pipe-lines or electrical conduits "protected" from corrosion by paraffin impregnated materials may be attributed in part to the activities of microorganisms which decompose hydrocarbons. Thin layers of paraffin are penetrated by *Botrytis cinerea*, and 17 other species of soil bacteria. It has been found that the soil mold *Penicillium glaucum*, can utilize paraffin as a sole source of energy. *Bacterium aliphaticum liquefaciens* is active on hydrocarbons ranging from *n*-hexane to tetratriacontane, $C_{34}H_{70}$ and some of the cyclic hydrocarbons as well. Growths can take place with *micrococcus paraffinae, mycobacterium album,* and *mycobacterium rubrum,* which will consume appreciable amounts of paraffin. The mold *Aspergillus versicolor* assimilates the hydrocarbon *n*-tricosane, $C_{23}H_{48}$ very well, but will not assimilate the larger molecule *n*-pentatriacontane, $C_{35}H_{72}$. Paraffin wax m. 45° was found to provide growth of soil fungi and bacteria better than paraffin wax m. 55°. The reader is referred to "Action of Microörganisms on Hydrocarbons" [*Bact. Reviews* **10,** 1–49 (1946), 182 references.]

Wax for Electric Condensers. An electric condenser usually consists of metallic plates separated and insulated from each other, *e.g.*, sheets of aluminum foil and wax paper. The amount of electricity that can be stored in the condenser depends upon the voltage, the size of the plates, their distance apart, and the nature of the insulator separating them. With higher voltage and larger plates more electricity can be stored in the condenser; and this ability to store electricity is measured by its *capacitance.* Capacitance is the important feature and not ohmic resistance. In condensers employed in electronic circuits the insulators between the plates are mica, hard rubber, waxed paper, air, etc. The dielectric constant or specific inductive capacity, of the material used as insulator between the plates or electrodes functions in direct proportion to the capacitance. Therefore, beeswax, which has a dielectric constant of 3.2, will not produce as high a capacitance as mica which rates at 5.6 to 6.4, though slightly better than ebonite which rates at 2.5 to 3.0. The unit (1.0) is the dielectric constant for air.

It is obvious that if a condenser of high capacity is to serve in a small space, a wax with a high dielectric constant must be chosen, with due regard also to the amount of voltage that can be impressed across dielectric, so as to avoid its breakdown. Electric condensers in the small sizes may be (*a*) *wax paper condensers,* or (*b*) *electrolytic condensers.* The *paper tubular condenser,* used so widely in radio circuits and in many types of electronic equipment, contains much wax. The *capacitor* in the paper condenser is composed of alternate sheets of very thin foil and wax paper; the pile is rolled into a small cylinder, *e.g.*, 1 cm diameter × 2.5 cm long and placed in a wax-impregnated tube with its wire terminals protruding. Each end is then filled with wax, termed *end-fill wax, i.e.*, a wax that will pour well at an elevated temperature, that will not interfere with the impregnating material in the capacitor, and that will be resistant to all possible climatic conditions to which the condensers are exposed. The complete assembly is given an overall dip in another wax, *e.g.*, paraffin and microcrystalline wax, to improve its moisture-proofness.

The impregnating material of the capacitor is generally *Halowax,* but any wax having a high dielectric constant, low power factor, and good chemical resistance can be used. The *end-fill wax* is usually a mixture of wax, a resin that will flow as freely as water when heated (Aroclor), and a filler such as powdered mica. The *overall-dip wax* is the same as the wax used for the tube impregnation, such as a microcrystalline petroleum wax of pale color and high melting point. An example of a tiny condenser used in a small electronic unit is one that only measures 150 mm in length by 25 mm in diameter, stamped with the rating "2000 ohms, and 20 Q" on the outside, and further identified by its red color for that size.

Electrolytic condensers are in a sense chemical condensers. There are hundreds of different kinds, some of which have liquid electrolytes and others solid. In general they depend upon the difference in electrical potential between the elements used in their make-up. A liquid condenser might be crystals of citric acid and glycerol; a solid one, wire electrodes insulated by a porous material impregnated with the electrolyte; or layers of foil and cambric folded zigzag and impregnated with sodium borate; or simply plates of metal with a layer of oxide. Electrolytic condensers are usually of larger size, (½ to 1½ inches in diameter) than the wax paper condensers. The casing is generally a molded plastic which has been wax impregnated in vacuum before assembly. When paper tubes are used to house the electrolytic elements the former must be moisture-proofed with wax in the same way as the paper tubular condensers. In some instances insulators are made of porcelain. A free flowing wax-resin mixture is used in the construction of the capacitor element, which itself is potted in the casing with pitch.

Electroplating Waxes. Waxes are of considerable importance in the art of electroplating, particularly when the object is to be produced in two or more metallic colors (such as nickel and brass) by electroplating, or the design is to be shown in both matte and bright areas. Wax is used as a "stop-off" for the electrolytic deposition of the metal or alloy in the affected area. It is also used in insulate the rack which holds the work, particularly where the work hung on the rack is made the anode for electropolishing; and deposition of metal on the rack is to be avoided while using the chemicals such as phosphates, borates, etc., as special electrolytes. A petroleum ceresin of 175/185° F melting point is of considerable value to the electroplater, although other high melting flexible waxes are also used.

Ratings for Insulation Waxes. Waxes for electrical insulation purposes are generally rated according to following constants:

(1) Water absorption
(2) Dielectric strength at 60 cycles
(3) Power and loss factors at 1000 kilocycles, with dielectric constant
(4) Melting point

A wax to be of value as an electrical insulator must show no water absorption when subjected to treatment with distilled water for 24 hours. Water absorption is then expressed as 0 per cent. The dielectric strength at 60 cycles is determined by A.S.T.M. Method D 149–40 T. For example, a wax may show an average of 62.6 kilovolts at puncture for an average thickness of 131 mils. Then the average dielectric strength would be 62,600 ÷ 131, or 470 volts per mil. A specimen of a synthetic wax had a power factor at 1000 kilocycles of 0.002; a loss factor at 1000 kilocycles of 0.004; and a dielectric constant of 2.20; according to A.S.T.M. Method D 150–41 T.

The electrical data are always considered in conjunction with the chemical data, *e.g.*, melting point, saponification value, acid value, ester value, and specific gravity at 25°.

Dielectric Constants of Waxes. Lee and Lowry,[78] of the Bell Telephone Laboratories, in 1927 reported their studies of the dielectric constants of insulating waxes, resins and bitumens, and the effect of moisture on such substances.

The following substances have a dielectric constant in the initial dry stage within the limits indicated:

2.0 –2.25	Paraffin
2.25–2.5	Candelilla wax, ceresin, ozocerite, paraffin, stearic acid, "Superla Wax"
2.5 –2.75	Montan wax, montan pitch, rosin, aluminum stearate, zinc stearate
2.75–3.0	Carnauba wax, Chinese insect wax, coumarone-indene resin, japan wax, beeswax
3.0 –3.25	Bayberry wax, manila copal, petroleum asphalt
3.25–3.5	Stearin pitch
3.5 –3.75	Paraffin-beeswax compound, spermaceti, shellac, "Halowax"

Dielectric constant not increasing more than 0.3 on six months' immersion test in 3.5 per cent NaCl solution:

Asphalt, beeswax, ceresin, candelilla wax, coumarone-indene resin, japan wax, montan pitch, montan wax, ozocerite, manila copal, paraffin, rosin, stearin pitch, "Superla Wax."

Dielectric constant greatly increased after immersion:

Aluminum stearate to over 4.9, bayberry wax to 10.4, carnauba wax to over 3.8, Chinese insect wax to over 3.6, "Halowax" to over 4.2, shellac to over 7.7, spermaceti to over 6, shellac to over 7.7.

All the waxes, and other materials tested, responded well to redrying, the dielectrical constants being restored to about as low or lower than the original dry ones.

Lee and Lowry also tabulated the "Effective A-C Conductivity" (Unit = 10^{-12} mho cm), initial, after immersion, and final (after redrying). They also tabulated the "Volume Resistivity" (Unit = 10^{13} ohm cm). A considerable amount of water is absorbed by some of the waxes. The natural waxes which contain fatty acids and esters absorb more water than the hydrocarbon waxes. Shellac, which is widely used as an insulating material in electrical apparatus, absorbs 4.3 to 5.1 per cent of water and loses its insulating properties to an appreciable extent.

Impregnating Wood with Paraffin. Hygroscopicity is one of the chief disadvantages in the use of wood. Shrinkage and swelling caused by moisture changes may be overcome by impregnating the wood with paraffin wax. Resistance to sulfuric acid is an important factor in determining the efficacy of paraffin wax treatment. Wax impregnated wood is of value for storage battery separators and other electrical insulation purposes, as well as for a host of non-electrical uses. Eberlin and Burgess[40] found that wood should not be dried before immersion in melted paraffin. They advised placing the wood in a tank of paraffin heated to 71° (160° F) and then raising the temperature gradually to 105° in about 30 minutes. Then the temperature is slowly raised, during 3 to 4 hours, to 135°. The wood is transferred to another paraffin bath at 71°; after 30 minutes it is removed, and its surface wiped free of excess wax.

Under the aforesaid conditions spruce wood will absorb 124 per cent paraffin, when using specimen board 11×100×92 mm. Wiertelak and Czarnecki,[129] at the University of Poznan, Poland, found 93.2 to 97.8 per cent absorption for the same size specimen of alder wood. They found that the major part of the absorption took place in two hours. The wood retains a considerable amount of moisture. The paraffin-impregnated wood resists comparatively well the action of sulfuric acid solutions. However, in two months' time the paraffin-impregnated board may take up as much as 26.5 per cent of storage battery acid. If dilute sulfuric acid solutions are to be handled there is less absorption, and the paraffin-impregnated boards may be safely used in building tanks and containers.

WAX FOR EXPLOSIVES AND PYROTECHNICS

Wax of some description occasionally is an ingredient in an explosive composition, but more often constitutes the water proofing agent for the explosive wrap.

Gun Powders. The gun powder manufactured in the United States is known as "A" or "B" blasting powder. These powders come in a variety of granulations. The "A" is used for black sporting powders, for making safety fuse, for pyrotechnics, and for quarrying dimensional stone. It is a mixture in suitable proportions of potassium nitrate, charcoal and sulfur. The "B" is made from the cheaper sodium nitrate, is of lower strength, and used mostly in mining coal. Granulated powder is also compressed into cylindrical pellets with a central perforation. These powder pellets are wrapped in a waxed cartridge paper, and fired by a fuse.

Dynamites. The majority of dynamites consist of nitroglycerin, which is a liquid, admixed with an absorbent of sodium nitrate and wood meal. Straight nitroglycerin dynamites are made in strengths of from 15 to 60 per cent liquid nitroglycerin. They have a relatively high rate of detonation, and therefore, are used wherever a quick action or a shattering effect is desired. Nitrostarch is also used in place of nitroglycerin, where it is necessary to have a non-freezing dynamite. Dynamites are of the nitroglycerin, ammonia, gelatin, ammonia gelatin, blasting gelatin, or other permissable types. All dynamite (except in large diameters) is packed in cartridge form by large, semi-automatic machines. The explosive charge is wrapped in paper, the ends of which are folded in and the resulting cartridge is coated with *paraffin.*

Paraffin or wax is seldom used in dynamite compositions. A milder and slower (phlegmatized) form of dynamite known as dynamite No. 2 does contain paraffin, and consists of nitroglycerin 18, uniformly mixed with potassium nitrate 71, charcoal 10, and paraffin 1 part.

Gelatin dynamites consist of a colloidal solution of guncotton in nitroglycerin, absorbed in a mixture of sodium nitrate and wood meal, whereas the normal dynamites contain no guncotton. The plastic consistency of gelatin dynamite allows it to be extruded through a nipple of the required diameter into *paraffin-paper shells* to form cartridges. Gelatin dynamite is waterproof and is used for wet work and under-water blasting. Pearsall[98] found that many advantages are gained by directly coating the cartridge with wax of a high melting point and dispensing with the paper wrap which often proves a source of trouble. *Petrolatum wax* serves the purpose well when used as a protective coating. The application of the wax can be taken care of by dipping the cartridge in the melted wax, or by other suitable means.

Blasting gelatin consists of nitroglycerin in which has been dissolved nitrocotton to form a jelly, together with a small proportion of anti-acid, such as chalk. Blasting gelatin is the strongest and one of the quickest explosives manufactured for commercial use, and the wrapped cartridges are paraffined.

Wax in Blasting Composition. An explosive suitable for blasting according to Sorenson[116] can be made from ammonium nitrate 100, manganese dioxide 15, *paraffin* 6, petroleum naphtha 6, rosin 15, potato flour 8, aluminum 30 and nitroglycerin 100 parts. Burrows[18] specified a mixture of barium nitrate 32, toluene 10, coarse aluminum 7.5, fine aluminum 0.5 part, with or without the addition of charcoal and *paraffin wax.*

Mining Powder. Palmer[97] specified a mining powder, claimed to be non-hygroscopic, powerful, and rapid, consisting of ammonium perchlorate 50, dinitrotoluene 14, sodium or potassium nitrate 31, aluminum powder 5, and *paraffin wax* 5 parts.

Nitrocellulose Powders. *Amberite* as manufactured by Curtis and Harvey, Tonbridge, England, contains on analysis the following ingredients: guncotton 13, collodion cotton 59.5, barium nitrate 19.5, a little potassium nitrate, paraffin 6, and volatile matter 2 parts.

Cordite. Cordite, the English Service propellant (produced in cords) is essentially a mixture of nitroglycerin and guncotton, thoroughly incorporated and gelatinized by means of acetone. "Vaseline," or crude mineral jelly, is used to stabilize it, prevent it from fouling magazine rifles by the bullets and as a waterproofing agent. Cordite does not ignite readily, but when once ignited it burns slowly with a strong yellowish flame, which is practically smokeless. Cordite is insensitive to shock, and burns explosively only when strongly confined. The ballistic power of cordite is four times that of black powder. The color of cordite varies from light to dark brown, according to the color of the mineral jelly used.

Cooling Agent for Smokeless Powder. Most smokeless powders have a high temperature of explosion, which not only causes erosion of the bore of the gun but also gives a strong and readily visible flame. To produce a flameless explosive Luciani[83] proposes the addition of a mixture of *carnauba wax*, *beeswax* and sodium bicarbonate to the smokeless powder.

Safety Explosives. A safety explosive manufactured by Curtis and Harvey, Tonbridge, England is known as "*Bobbinite.*" It is really a high grade gunpowder containing but little sulfur, with ingredients added to increase its safety. As originally made, according to Thorpe, it consisted of niter 64, sulfur 2, charcoal 19, and a mixture of ammonium sulfate and copper sulfate 15 parts. The sulfates were later replaced by starch 8, and *paraffin wax* 3 parts, other constituents being correspondingly increased. The mixture is compressed into pellets, which are then coated with paraffin wax. "Bobbinite" is safe to handle and is fired without detonators; it is slow burning and not dangerous in fiery mines.

Shell Powder. Shell powder may be prepared, according to Bowen,[13] from ammonium perchlorate 75, aluminum powder 12, and *paraffin* 13 parts. The powder matte if extruded through bronze dies requires *candelilla wax* or its equivalent to lubricate the dies.

Fuses and Detonators. Wax emulsions having *carnauba wax* as the principal wax constituent are used for waterproofing fuses and detonators. The same emulsion is used in waterproofing powder bags in the Navy. Yellow amorphoid hydrocarbon waxes of 160–165° melting point are also said to find an extensive use for such purposes. *White bleached beeswax* is employed to some extent.

T.N.T. Explosive. Burrows and Burrows[17] prepared an explosive consisting of a mixture of ammonium perchlorate 6, potassium nitrate 56, aluminum 18 and trinitrotoluene 18 parts, to which they further added 2 parts of refined paraffin wax. The aluminum is prepared by pouring the molten metal on a rapidly revolving wheel which dashes it in a spray into cold water, thus producing large particles with sharp points susceptible to rapid ignition. The α- or 2,3,4-trinitrotoluene is that obtained by the distillation of the so-called liquid trinitrotoluene and is known as "tolite," "trilite," "trinol," and "trotyl."

Phlegmatizing Wax for Explosives. A wax of a suitable kind is incorporated with an explosive material when it is desired to reduce the speed of explosion. Its customary function is to provide a less intimate contact of the particles of the explosive with one another. *Phlegmatizing waxes* may be roughly classed as *A*, oxygen containing, such as fatty esters and ketones; or *B*, non-oxygen containing, such as paraffin and ceresin. An instance can arise where a wax of class *B* is not compatible with the explosive material, necessitating the use of a wax of class *A*, as in phlegmatizing tetranitropentaerythritol; or on the other hand an instance where *A* is undesirable because of its oxygen content, and the use of *B* is advantageous because of the release upon firing of hydrogen atoms, which function as the slowing barrier. Paraffin is known to act as an agent for absorbing neutrons, and is used for protecting personnel working on atomic energy research. Phlegmatizing waxes are also occasionally used in pyrotechnic material.

In World War II, the German military employed a phlegmatizing wax in their tetranitropentaerythritol and R.D.X. explosives for their African campaign. A suitable wax was found in a ketone of 90° melting point obtained by heating together a mild oxidation product of montan wax, and a long chain hydrocarbon (I.G. Wax Z) which had been partially converted to a wax acid by the Fischer-Tropsch process, using a potassium permanganate catalyst. In the latter process the oxidation was stopped when the acid value reached 40 to 45, and the melting point about 80°. The waxes that were fused together to prepare ketone were known as *I.G. Wax L*, and *Emulgier Wax P.S.*

Paper Shot Shell Tubes. These shell tubes are impregnated with *paraffin wax*. Schilling and Latham, Remington Arms Co.,[106] claim that if the paraffin wax is kept at the impregnating temperature, 230–240° F (110–115.5°) in a tank for an extended period, acidic decomposition products are formed, and their presence not only interferes with the proper penetration of the wax into the paper tubes, but thereby decreases the resistance of the paper tube to burning powder. If the powder burns through the tube, failure of the tube will result, and upon extraction of the fired shell from the gun, a part of the tube will be left in the barrel. The degree of the decomposition may be measured by determining the saponification of the wax. The decomposition of the paraffin can be arrested by the addition of a small amount of poly-alkylated phenols; *e.g.*, 2,6-dimethyl and 2,4,6-trimethyl phenol.

It was found that if a crude scale paraffin wax was heated for 72, 141, and 230 hours, the saponification values were 10.0, 14.0, and 29.0 respectively. By adding 0.50 per cent of the inhibitor to the paraffin to begin with, these values came down to 0, 0, and 0.5 respectively. A standard practice is to keep the saponification values below 10 or 12. This can be accomplished by adding fresh wax to the tank at frequent intervals, but it is a simpler matter to use an inhibitor. To be effective the quantity added should be at least 0.2 per cent.

Cartridge Cases. In the preparation of cartridges having metal cases, it has been found desirable (according to Pedersen,[99] of Springfield, Mass.) to apply to the metal case a relatively thin coating of some protective substance which will preserve the metal case for comparatively long periods of time against deterioration, such as seasonal cracking. It is also desirable to choose a coating which will perform the additional function of acting as a lubricant for the case of the cartridge, for facilitating introduction into the chamber of the gun and extraction thereof after firing.

The most suitable wax found for waxing metal cartridge cases according to Pedersen is *ceresin*, a refined product of ozocerite. This is because of the hard and non-tacky properties of ceresin at ordinary temperatures, and its melting point range between 140 and 176° F. It is smooth and glassy when hard and does not gather dirt or dust. When the ceresin on the cartridges is melted in the chamber of a gun, it becomes a lubricant.

In applying the wax to the batch of cartridges, it is desirable to preheat the cartridge cases to approximately the same temperature as that of the heated bath of the wax solution, in order to secure a uniformly thin film, and to accelerate the drying or evaporation of the solvent. The latent heat in the cartridge case, because of the preheating, is effective in drying out the coating film and speeding up the waxing operation as a whole.

In the Pedersen process about 7 per cent of *ceresin* is dissolved in carbon tetrachloride, and the solution is then heated to approximately 100 to 120° F. The cartridges are likewise heated to the same temperature so that there will be no heat exchange in the application whether by dipping, spraying or brushing. The dipping process is preferred. The process can be made a continuous one in which the cartridge cases pass on a conveyor through a drying oven, into the heated liquid bath and out through a current of heated air to vaporize the solvent. Instead of ceresin (ozocerite) a petroleum ceresin wax can be used.

Pyrotechnics. Pyrotechnics are fireworks that are mainly for display purposes, such as rockets, Roman candles, etc. Firework displays were well known in China for many centuries, prior to their introduction in Europe. Pyrotechny is essentially a handicraft. All fireworks contain a combustible substance, and a supporter of combustion. The combustible is referred to as the fuel, and may be sulfur, carbon, resin, starch, picrates, etc. Powdered metals are included. The supporters of combustion are mainly oxygen salts, such as chlorates and nitrates. The mixtures used in pyrotechny are called fuses. In some instances, such as the fuses for blue fire, *paraffin wax* is used with potassium chlorate as the combustible substance. For white lights the following composition may be used: barium nitrate 36–40, strontium nitrate 6–8, magnesium 50–54, and *paraffin wax* 2–4 parts. Color flame effects can be obtained from barium nitrate and particles of a magnesium or aluminum bronze alloy with 1 per cent of liquid wax. A signal torch or flare has been made from strontium and potassium salts, lacquer, sulfur, sawdust, *petrolatum* and *paraffin wax.*

The greatest use of wax in the pyrotechnic industry is in the waterproofing of the cartons in which the fireworks are shipped.

WAXES FOR FLOORS AND FLOOR COVERINGS

The floor being the integral part of the interior of a building which must withstand most of the wear, it is logical that it should receive especial attention and care. The application of waxes to wooden floors, such as parquet floors, for the purpose of their preservation dates back centuries. Many floors are covered with a soft pliable material, such as linoleum, rubber tile, and congoleum, which is cemented or otherwise fixed to the original flooring. Quite often a layer of felt is laid between the under flooring and the floor covering to act as a cushion. The application of wax to such flooring material retards the penetration of air and moisture, thereby increasing the life of the cushioning material as well as preventing deterioration of the surface by abrasion from grit.

Wood floors should have a foundation coat of paste wax after a thorough cleaning, although subsequent waxing may be carried out with a liquid floor polish, in which the solvent is of a type that will tend to cleanse as well as leave a film of wax which may be rubbed to a high luster. Paste waxes are preferred where power machines are used on the floors. A paste wax is semisolid at ordinary room temperatures and contains about 30 per cent of nonvolatile matter. The solvent may be the same as that used in liquid wax.

Classification of Floor Waxes. Floor waxes may be classified, for convenience, in the following manner:

(1) Solid floor waxes
    (*a*) In paste form
    (*b*) In powdered form
(2) Liquid floor polishes
    (*a*) Rubbing polish
    (*b*) Non-rubbing polish
    (*c*) Mop oil

Floor waxes are mixtures of waxes of various degrees of hardness with a suitable solvent, with or without the addition of coloring matter. The principal ingredients are proportioned so that the resultant product will conform to specifications required as to appearance at the time of use, and performance in polishing floors or floor coverings.

Specification Requirements of a Floor Wax. There are a number of essential requirements that must be considered by the manufacturer of floor waxes before he can successfully market his product. The specification requirements are based upon:

(1) Odor, appearance and color
(2) Degree of luster obtainable after application to the floor
(3) Wearing quality of the wax foundation
(4) Condition of both material and container after prolonged storage
(5) Consistency of material relative to its removability from the container
(6) Ease of application to the floor
(7) Drying time of polish film after application
(8) Flexibility of polish film
(9) Freedom from water-spotting
(10) Washability with soapy water or with mild detergent
(11) Marproofness of wax film to light scratching
(12) Freedom from slippage
(13) Area of coverage per pound
(14) Cost of manufacture per pound

Solid Floor Wax. (Paste Form). Solid floor waxes are made up of carnauba wax or its equivalent together with softer waxes such as paraffin or ceresin, and a semi-hard wax such as bleached montan wax, the waxes being combined with a suitable solvent, often mineral spirits and turpentine. The principle involved is that the carnauba wax furnishes luster, and hardness, and that the softer waxes give the paste its consistency and solvent retention. In general the solid floor waxes in paste form comprise 31 per cent of solid waxes, and 69 per cent of solvent, *e.g.*, white mineral spirits mixed with turpentine. Mineral spirits is the name given to a refined petroleum distillation product that has a boiling point range fairly close to that of the balsam spirits, or turpentine.

The content of carnauba wax in a floor wax is not as high as that in an automobile polish, and in general does not exceed 12 per cent. An automobile polish requires a high wax content (18 per cent) because it is used for polishing metal surfaces. Since floors of wood absorb paraffin too freely it is necessary to keep the paraffin wax content down to 10 per cent or less. For example, a recipe for a floor wax may well read: *Carnauba wax* 12, *bleached montan* 5, *hard petroleum ceresin* 3, *paraffin* (m. 130° F) 11, mineral spirits 60 and turpentine 9 parts. Another recipe for a floor wax calls for *yellow beeswax*, *ceresin wax*, *carnauba wax*, *montan wax*, and mineral spirits with a little turpentine and pine oil added.

The appearance of a solid floor wax in its container should be that of a paste with a smooth and glossy surface, and of uniform consistency. Beeswax and the high melting point hydrocarbon waxes improve the smoothness. The use of IG Wax OP is also effective in the same respect. Rapid cooling of the paste after filling aids the appearance. The odor of floor wax is regulated by the addition of alpha terpineol, or any perfume which will give the wax a clean, pleasing, sanitary odor. The preferred colors appear to be yellow and orange and only oil-soluble colors are used.

Waxes that gel well to begin with may later produce fissures in the paste due to poor solvent retention, and this must be kept in mind when formulating solid floor waxes. Ease of application and spreading is brought about by using waxes free from stickiness and containing a solvent which will not evaporate too rapidly, although the softer waxes also inhibit rapid drying, paraffin wax notably so.

The luster of the applied wax film is directly associated with those waxes which are of natural plant origin, namely *carnauba*, *ouricuri*, *candelilla*, *esparto*, etc., assisted by the presence of semi-hard waxes such as montan or extra hard paraffin. *Beeswax*, *ozocerite*, and *petroleum ceresin wax* lend plasticity to the wax film and tend to reduce slippage. The incorporation of *calcium* or *magnesium stearate* in the wax foundation of floor waxes has met with favor, since they assist in preventing undue marring and slippage, and make the polish film resistant to water-spotting and to repeated washings by soapy water and mild detergents. The slippage of wax can be determined by means of a testing machine as described by Fuld.[48] The machine operates on an oblique-thrust principle. Fuld stated that the coefficient of friction for various floor waxes varies from 0.1623 to 0.3000, and that the maximum slippiness of a wax occurs three days after its application.

Oil Uptake of Waxes.

Binding Power and Consistency of Gel for Waxes with Turpentine

One Part of Wax to 2 Parts of Turpentine (1 g to 2 ml)

Kind of Wax	Binding Power	Consistency of Gel	Texture
Beeswax	poor	soft ("Vaseline"-like)	smooth
Candelilla	good	medium soft	fairly smooth
Carnauba	excellent	very firm	grainy (dull mat surface)
Ceresin	fair	medium soft	smooth
Esparto	excellent	very firm	grainy
Halowax	very poor	soft	very fibrous
IG Wax OP	excellent	very coherent and firm	smooth and mirror surface
Japan	poor	very soft	smooth
Montan, bleached	excellent	firm	smooth
Myrtle wax	very poor	soft	grainy
Opalwax	fair	soft	grainy
Ouricuri	very good	firm but bleeds under pressure	somewhat grainy
Ozocerite	very good	fairly firm	smooth
Paraffin	very poor	very soft	smooth
Peanut Oil, hydrogenated	very poor	very soft	grainy
Petroleum Ceresin	poor	soft ("Vaseline"-like)	smooth
Rezo wax	very good	firm	very grainy
Spermaceti	very poor	liquid	liquid
Sugar Cane Wax, refined	good	quite firm	grainy
Utahwax, crude	very poor	soft	lumpy
Vegetable Wax, Synthetic (greenish yellow hard wax)	excellent	very firm	grainy (ring surface)
Calcium Stearate	fair	quite firm	shrinks

Lux[84] has reported on the oil uptake of waxes in a numerical manner. A solution of 22 parts of pure refined ozocerite, m. 75°, and 78 parts of oil of turpentine (sp. gr. 0.9800) were used as a standard for determining the amount of solvent necessary to produce a paste of similar consistency from various waxes. Penetration at 20° of a flat-surfaced sinker was used for measuring the consistency.

Number of parts solvent per 100 parts of wax that will give the same consistencies:

Ozocerite (m. 75°)	354
Petrolatum Wax (m. 65°)	233
Paraffin Wax (52/54° solid. pt.)	426
Carnauba Wax, crude	900
Montan Wax, crude	525
Kara Wax	614
I.G. Wax OP	1600–1900

There is a noticeable difference in the solvent retention of the different kinds of waxes. A comparative test may be made on the following basis: two grams of wax are melted and dissolved in four milliliters of turpentine, and the mixture cooled to 20°, and then warmed to 25°, at which temperature it is maintained. The small glass beakers holding the wax mixtures are left uncovered and weighed periodically. Measurements of loss of solvent are accurate to 0.5 per cent.

Loss in weight of wax gels due to solvent evaporation:[127]

	Loss in			
Type of wax	24 hrs (%)	48 hrs (%)	72 hrs (%)	7 days (%)
Carnauba	5.5	9.2	16.5	34.9
Ouricuri	0.5	11.0	20.0	41.5
Candelilla	0.5	1.8	3.7	5.5
Esparto	3.6	7.3	11.0	23.4
I.G. Wax OP	0.5	7.3	14.7	39.7
Petroleum Ceresin	3.6	7.3	9.0	18.0
Paraffin	0	0	0	0
Japan	5.5	12.6	20.0	32.5
Calcium Stearate	7.3	14.7	23.5	45.2
Stearic Acid (triple pressed)	0.9	1.8	3.6	9.0

Note: Carnauba wax gel cracked at edge, I.G. Wax OP gel developed fissures, paraffin wax remained very soft, japan wax gel cracked, and calcium stearate gel showed much shrinkage.

Use of I.G. Wax OP in Paste Waxes. The use of I.G. Wax OP in a solid floor wax imparts a number of desirable qualities. It not only hardens the paraffin constituent but produces an excellent gel with the solvent, even when used in small quantity. It gels with turpentine to a remarkable mirror-like surface, and imparts some of this characteristic to the paste compound. Although it has an excellent turpentine uptake, it is somewhat deficient in its solvent retention, and might cause cracks if used in too high a concentration in the paste. Paraffin, on the other hand, has a poor oil uptake, but has an excellent solvent retention power. Hence the combination of much paraffin with a small amount of I.G. Wax OP will gel and retain the solvent well. The combination permits a reduction in the amount of carnauba wax in a given recipe, and an increase in the paraffin content, making it possible to lower cost without reducing quality.

An example of a recipe for floor wax which specifies I.G. Wax OP is of the following order: *carnauba wax* 8, *ceresin* 15, *bleached montan* 2, *paraffin* 24, *beeswax* 4, *japan wax* 4, *OP Wax* 1, turpentine 50, and white mineral spirits 90 parts. It will be noted that in this recipe the non-volatile content is 29 per cent, and the carnauba wax content only 4 per cent. For waxing linoleum floors a little higher wax content (4–10 per cent) of carnauba wax is desirable. The value of beeswax and of japan wax in the above recipe is open to question.

In melting the waxes for the manufacture of floor polishes overheating must be carefully avoided to prevent disturbance of the grain structure. The white mineral spirit is very slowly added in a thin stream with constant stirring while the wax melt is kept at a temperature of 90°. The heating must be shut off before adding the solvent. The solvent may have small quantities of dipentene or dehydrin added to it, which give the solvent a balsamic odor. The pouring of the floor wax in the large tins is done at a temperature of 40 to 45° (104–113° F). The large flat tins are first partially filled and the polish is cooled and then the tins are filled to the brim so as to avoid a depressed surface. When filling smaller tins double filling may be avoided by pouring the polishing wax at the lowest possible temperature. The pouring vessel used should be insulated so as to hold the wax at a constant temperature.

Liquid Floor Waxes. Liquid floor waxes have the same foundation base as the solid floor waxes, but very much more solvent, so that the wax or non-volatile content may amount to only 8 to 15 per cent in the polish. It is also customary to use less volatile spirits for the solvent. The Standard Oil Company of New Jersey markets suitable solvents for such a purpose, namely Panoline and Mineral Seal Oil, which can be used with a lesser amount of mineral spirits or varnolene. A paste floor wax can be converted into a liquid wax by the addition of such prepared solvents.

Artificial waxes such as *Rezo Wax B* have been used effectively with paraffin waxes as a means of producing a gel dispersion with a non-volatile content of 34 per cent in the finished product. The use of stearates in polishes has come into vogue, particularly *calcium stearate*, *barium stearate*, and *zinc stearate*. In pastes the stearates have the disadvantage of being shrinkable if used in any appreciable amount. Deguide[35] gives a recipe for a composition suitable for polishing floors as, *barium stearate* 55, *paraffin* 28, and a hard wax (*carnauba* or equivalent) 17 parts, colloidally dispersed in spirits of turpentine in a stable gelled condition.

Rubless Floor Polishes. A rubless polish is usually a translucent wax and water emulsion which gives a film of high brilliance with little or no rubbing when spread over a surface and allowed to evaporate. A rubless polish has advantages over wax and solvent rubbing polishes in the following respects: (1) it is more easily applied, (2) it does not need the application of polishing equipment, (3) it is subject to less adulteration with inferior polishing agents, (4) it eliminates the fire hazard attached to storage in warehouses or on shipboard. On the other hand rubbing polishes have the distinct advantage that the rubbing coat may be applied without scrubbing off the old wax; the need for water and soap cleaning is eliminated. Wooden oak floors may be marred and linoleum dried out as a result of repeated cleansings with alkaline powders.

A rubless polish may be used in the sprayer of a vacuum cleaner, which is generally equipped with a sprayer jar that can be filled with the liquid polish, a sprayer nozzle attached to a hose, and a valve, which controls the spray of polish from the nozzle in a fine mist at a distance four to 5 inches from the floor surface. The film is water repellant and its resistance to wear increases for several hours after application of the polish. This type of polish is also referred to as self-polishing, washable, liquid floor wax.

A recipe for a rubless polish is the following: *carnauba wax* 13.2, oleic acid 1.5, triethanolamine 2.2, sodium borate 1.0, water 99.0, shellac 2.2, and ammonia water (28 per cent NH_3) 0.32 parts by weight. Melt the wax and oleic acid, using a hot water bath or steam jacketed kettle to heat mixture to 90°. Add the triethanolamine slowly, stirring constantly until the solution becomes clear. Dissolve the sodium borate in a part of boiling water and add it to the wax solution. Stir the resulting clear mass for 5 minutes. Add 47 parts of boiling water slowly with constant, vigorous agitation until a smooth dispersion is obtained. Cool, and add 16 parts of water and the ammonia to the shellac and warm until solution is complete. Cool and add this to the wax dispersion. Finally, stir in the remaining 52 parts of water at room temperature.

The following is a recipe in which an organic amine, $O(C_2H_4)_2NH$, known as Morpholine is employed as the emulsifying agent. The latter boils at 128 and has the density of water. Carnauba wax 11.2, oleic acid 2.4, Morpholine 2.2, water 67.0; shellac 1.5, Morpholine 0.2, water 15.5 parts by weight. Melt the wax and the oleic acid, add the Morpholine, and stir until clear. Slowly add the water, previously brought to a boil, to the hot wax mixture with constant stirring, each small portion being well incorporated before further addition. The mixture becomes increasingly viscous when two-thirds of the water has been added. The mixture then begins to thin out and the remainder of the water may be added rapidly. The total period of water addition should be 30–40 minutes. A steam-jacketed kettle and a hand-operated paddle, or a slow speed large-bladed propeller are recommended for successful production. After cooling the product while slowly stirring, the shellac solution is added.

This has been made by warming together the Morpholine, water, and shellac of the second part of the formula. The polish is then filtered if necessary. It is desirable to have the receptacle holding the finished polish equipped with a portable electric stirrer, so that the emulsified polish can be kept in a state of agitation at the time of filling to give a perfectly homogeneous product.

Wax-soap Type of Emulsions as Floor Polishes. In the wax-soap emulsions and paste preparations used in waxing floors one or more of the following waxes are used: *paraffin*, *beeswax*, *montan wax*, *carnauba*, *japan*, *candelilla*, and *shellac wax*. The latter is obtained as a by-product in shellac purification.

According to Tyler the water-emulsion type of floor wax is used on newer types of flooring such as rubber where a volatile solvent wax is not suitable. Too much soap reduces the luster and the resistance of the wax film to water. He gives successful formulae of the following order: (*A*) Sodium soap 0.9, *carnauba wax* 8.8, shellac 3.6, borax 0.7, water 86.0 parts. (*B*) Sodium soap 1.7, *carnauba wax* 8.7, shellac 1.3, borax 1.4, and water 86.9 parts.

Mop Oils. Mop oils are made from mixed waxes, spindle oil, and turpentine, with or without the addition of mineral spirits, and are frequently artificially colored and scented. For example, to produce a mop oil 3 parts of waxes may be dissolved in spindle oil 70 parts, and a mixture of 30 parts of turpentine with mineral spirits. The combination of waxes would be the same as that used in solid floor waxes.

Wax Floor Powders. Wax floor powders are made particularly for waxing dance floors. They can be produced by finely pulverizing a mixture of damar resin with wax in about equivalent proportions. The wax may be a soft wax such as *paraffin* and a hard polishing wax as *carnauba*. Batavia Damar, Pale East Indian Resin, or Batu Bold (scraped) are the resins used, as they are compatible with carnauba, paraffin, or other selected waxes. The wax is first melted and then the resin added; the combining temperature is 130 to 140° when using Batavia Damar but somewhat higher for the Batu Bold.

The stearates, such as *calcium stearate* and *zinc stearate* have been incorporated in dance floor powders. *Aluminum stearate* is now being used to improve the body and smoothness of the floor and to prevent slippage. In some formulations talcum is incorporated in the molten wax. With talcum, the wax is more easily powdered, the floor coverage per pound is increased, and the waxed surface is better preserved under wear.

Formulation of Resin-wax Polishes. The American Gum Importers Association have published certain recipes for no-rub polishes in which a carnauba wax emulsion is mixed with about an equal proportion of Manila resin solution in a so-called formula P–183. The Manila resin solution is prepared from 30 pounds of Manila DBB, 19 gallons of water, and 12 pounds of ammonia water (28 per cent NH_3). The carnauba wax emulsion consists of 30 pounds of *carnauba wax*, 25 gallons of water, 5 pounds of Trigamine, 3.5 pounds of oleic acid, and $\frac{1}{4}$ pound of caustic soda. In the latter recipe the wax and oleic acid are melted together on a boiling water bath, the trigamine stirred in, and a boiling 4 per cent caustic sodium hydroxide solution slowly stirred in. A gel forms and the remainder of the water (boiling hot) is added. The finished polish is a mixture of 39 pounds of Manila resin with 34 pounds of the carnauba wax emulsion.

A similar formula employs a carnauba wax emulsion of 30 pounds of carnauba wax No. 1 yellow, 25 gallons of water, 3 pounds of triethanolamine, and 5 pounds of oleic acid. The Manila resin solution consists of 30 pounds of Manila DBB, 19 gallons of water, 12 pounds of ammonia water (28 per cent NH_3). The finished polish consists of 34 pounds of the wax emulsion with 39 pounds of the Manila solution.

A formula P-185 employs a thermally processed Congo melted down with the carnauba wax, and then emulsified with caustic soda, triethanolamine, and oleic acid, finally adding the required amount of water.

Natural resin-wax polishes may be made by melting paraffin and carnauba, sifting in pale East India resin, and thinning out with turpentine (Formula P-186) or with VM & P naphtha (Formula P-187). East India resin may be formulated with beeswax, carnauba wax, montan wax, VM & P naphtha, turpentine, and a little pine oil for a gloss polish (Formula P-188). Pale East India resin 18, carnauba wax 15, paraffin 17, turpentine 35, and VM & P naphtha 35, constitute a formula, P-189. A solid floor polish (formula P-190) is made from petrolatum wax 45, East India resin 45, and paraffin 10.

Waterproofing Building Material. There is need for a wax composition that will be useful and economical in waterproofing and weatherproofing buildbuilding material such as brick, cement, stone, terra cotta, and wood. The composition used must take care of the discoloration that results by efflorescence of salts dissolved out of the building material. An example of a proposed waterproofing composition is Chinawood oil 22, *paraffin wax* (m. 122° F) 13, japan drier 0.1, naphtha solvent 64.9 Such a composition however is too costly.

Baldeschwieler and Gaylor[7] propose a less expensive composition than that given above, and one which they claim has excellent waterproofing qualities for building material. The composition is formed of paraffin wax together with 10 to 20 per cent of a drying petroleum oil made by cracking a petroleum oil at temperatures of about 700–1200° F. Their prescribed formulation is given by the following example: paraffin wax (m. 122° F) 13, cracking oil tar 15, japan drier 0.1, and heavy naphtha solvent 65 parts. Coating compositions of this kind may be applied to the material by brush or spray.

Wax in the Food Industry

The most important use of wax in the food industry is in its application to the art of impregnating or coating paper materials for wrapping or packaging foods. This particular subject will be covered on p. 433 of this chapter.

The next important use of wax, from the standpoint of wax consumption, is in the waxing of fresh fruits—an industry which is growing steadily. The employment of wax as a protective coating or covering for cheese is an extensive one. Other uses, some of which are only of minor importance, are described here; *e.g.*, the wax coating of sausage, the incorporation of wax in doughnuts and candy.

Wax Coating Cheeses. It is customary to prepare cheese in the form of blocks or cylinders of varying sizes, such as midgets, twins, daisies, cheddars, wheels and longhorns. After the curd has been in the mold under pressure a sufficient time to permit it to set, it is removed and placed in a cooler at a temperature of 4.5 to 7.5° (40–45° F) for from one to two days until a partial rind has formed on the surface. The molded cheese is generally dipped in molten hydrocarbon waxes at about 110° (220° F) to form the protective coating on the surface. This coating keeps the cheese from drying out, and prevents mold growth from developing on the surface. In the manufacture of cheddar cheese, the curd is normally pressed in a mold, the mold having first been partially or wholly lined with cheesecloth. The cheese is then handled as are other cheeses. It has been found that Danish cheese of the cheddar type when paraffined after several weeks of curing gained 0.4 per cent in weight. The shrinkages in weight for periods of 30, 60, and 90 days were 0.3, 1.7, and 3.2 per cent respectively; and for unparaffined cheese used as control 2.9, 5.1, and 7.5 per cent. It has also been found that less shrinkage occurs where the *paraffin* has been admixed with a *microcrystalline petroleum wax.*

Red Coating for Ghouda Cheese. A Ghouda cheese is coated through custom with a red colored wax. After the cured cheese is at least ten days old, it is washed with warm water containing 1 per cent of ordinary blue-lime, dried thoroughly, and dipped in the prepared paraffin wax mixture heated to 150° (300° F). This mixture consists of *paraffin wax* 85, petrolatum 5–10, *ceresin* 1–1½, and oil-soluble carmine-red dye 2–3 parts. The red wax envelope is easily removable from the sliced portions of the covered cheese.

Translucent Coating for Cheese. Many cheeses are coated with translucent waxes. A *white scale wax* (m. 124–130° F) 85, and *white petrolatum wax* 15 parts, make a satisfactory wax composition for coating ordinary cheeses.

Ennis[48] advanced the idea of double coating certain types of cheeses; that is, giving the cheese a dipped coating of a mixture of *paraffin* and *microcrystalline petroleum waxes,* and thereafter a secondary coating of paraffin wax, to which yellow or other desired color is added. This method has been reduced to commercial practice. Ennis refers to a suitable composition of the primary coating as: *microcrystalline petroleum wax* (m. 160° F) 60, and *paraffin wax* 40 parts. The redipping may also be effected with micro wax 20–30, and paraffin wax 70–80 parts. For the secondary coating scale wax is for some purposes the preferred wax, and the treatment of the cheese is carried out just above the melting point of the wax.

Peelable Coating for Cheese. Ingle and Mink[67] have proposed a coating for cheese which will not become tacky in warm temperatures, check or crack at low temperatures, and one which can be readily peeled from the cheese surface cleanly and without breaking. The coating consists of a synthetic hard brittle resin made from rubber which is incorporated in paraffin or other suitable wax. The synthetic rubber resin is a reaction product of the treatment of rubber with an amphoteric halide described in one of their patents.[66] In preparing the wax coating for cheese the paraffin wax is heated to 220° F, and about 10 per cent of the finely divided synthetic rubber resin added; heating is discontinued and the mixture is agitated until it begins to thicken, and is then allowed to stand from 15 to 30 minutes. The rubber resin swells at first, and when the mixture is reheated to about 220° F a homogeneous liquid mass is formed, suitable for the coating operation.

Wax Coverings for Cheeses. In packaging pasteurized or processed cheese, the cheese is wrapped in a protective film or sheet, such as a wax coated cellophane. The cellophane is most often printed in colors, then the coating of wax applied by a pick-up roll to the unprinted side, whereupon the wax coated cellophane is cooled and rolled up. The wax is one containing rubber and paraffin in its composition, for example, *Sealz-3008* of the Dispersion Process, Inc. With the wax next to the cheese, a protective coating film is formed; this skin adheres to the cheese, precludes loss of water and flavor from the cheese, and prevents bacteria and molds for getting into it from the outside sources. This method of protecting fine quality packaged cheeses is proving highly successful in a commercial way.

Pliowax (a compound prepared from paraffin and a cyclized rubber resin of the Goodyear Company) has been recommended as a coating for cheese, since it does not crystallize at refrigerating temperature and prevents loss of moisture from the cheese. Pliowax has no effect upon the taste or odor of the cheese. It may be stripped off more readily and replaced after part of the cheese has been used. Many thousand pounds of cheese have been coated with Pliowax and this type of coating is adaptable to other food products as well.

Ingle[65] invented a means of inhibiting the growth of mold on cheese, by incorporating in the wax a suitable amount of propionic acid through the agency of the addition of a small amount of a higher fatty acid. A typical example of a wax which is particularly effective in coating cheese wrappers contains 0.3 per cent *stearic acid*, 3 per cent propionic acid, and the balance *paraffin* or other wax composition. The coating should be applied to the surface of the wrapper which comes in contact with the cheese, but may be applied to both surfaces, if desired.

A vent wrap for packaging cheese has been described by Abrams and Wagner.[2] The method of packaging comprises completely enclosing the cheese with a film of wax-rubber composition, then applying a wrap of comparatively gas-impermeable material, sealing the seams of the outer wrapper but providing a vent whereby a portion of the gas generated during the curing of the cheese will be retained as an atmosphere about the cheese, and the excess gas permitted to escape. This type of package is said to protect the cheese from mold growth, loss of moisture and development of bitter flavor.

Wax Wraps for Frozen Fish. Frozen fish is wrapped in waxed parchment paper, or in "refrigerator locker paper" (see p. 434). Large fish so wrapped is inserted in a "stockinette" of suitable size, which is then tied securely. Smaller fish, fillets and steaks are individually wrapped in moisture-proof cellophane, or coated vegetable parchment, and then placed in a proper size folding carton, which has been heavily waxed with *paraffin wax* to which a small proportion of *petrolatum wax* has been added. After closing the carton, it is advisedly overwrapped and heat-sealed in moisture-proof paper or cellophane. Cured meats are packed in a similar manner to fish (see Packaging of Frozen Foods, p. 434).

Wax Coatings for Sausage. Dry sausages are cured by stuffing into casings fresh comminuted meat mixed with curing ingredients, and coating the uncured individual sausages with wax, then maintaining the coated sausages at drying temperature until cured. Generally hot paraffin is used for the waxing. The preserving of sausage has two important aspects: resistance to spoilage and putrefaction, and retaining the organoleptic factors such as flavor, color, texture, etc. The wax treatment imparts a better color and surface appearance to the unsmoked dry sausage. A wax coating is recommended for Polish sausage; but it must be applied only on sound, clean, well-aerated sausage in which the gas evolution after preparation has been fully completed. Wax coating is found to be the most effective means for maintaining the quality of salami for prolonged storage, and the best packing medium for shipment is finely chopped oat straw.

In the process of Kellermann[72] the sausages are coated with *paraffin* which has been heated to 93° (200° F), and then applied by dipping or spraying. After the wax is set, the sausages are transferred to the standard drying room, where they are hung on racks to permit circulation of air around each sausage. The sausages remain in the drying room which is held at ordinary room temperatures, until they are cured and dried. The former method without waxing was to cure the sausages in a "green room" which was warm and humid, and then after a few days to transfer them to the drying room which was cool, and cure them for 2½ to 4 months. In the wax method of curing the "green room" can be dispensed with, and the curing in the dry room takes 3 to 4 months. Ennis[43] recommends dipping the sausage in a blend of *paraffin* and *microcrystalline petroleum waxes*, and then redipping in *paraffin wax*.

Wax in Doughnut Sugar. A prepared sugar for dusting doughnuts to complete their manufacture has been patented by Schlegel and Lang.[107] They specify the incorporation of about 0.4 per cent of *beeswax*, *carnauba wax*, or *sugar-cane wax* with powdered sugar to obtain a food-dusting sugar. The object is to render the doughnut grease and moisture repellant, thereby maintaining a fresh appearance to the finished doughnut.

In its manufacture the sugar is placed in a steam jacketed stirring receptacle of the kind having an inside stirrer and scraper, and supplied with steam at about 10 pounds of pressure, which raises the sugar to a corresponding temperature above the melting point of the wax, but not sufficient to melt the sugar. The wax is melted and introduced into the receptacle, which is covered, and stirred until all outward evidence of the wax has disappeared. Each individual crystal or particle becomes coated with a thin film of wax without having its appearance altered. A test for sufficiency of wax coating is to put a spoonful of the prepared sugar in a glass of water on the surface of the water; it should not sink. It can, however, be stirred into the water to give a clear solution. Incidental to the non-absorption of grease, a lighter dusting is required and that is an economic consideration. The taste of the prepared sugar containing the wax is identical to that without wax. Thus far *beeswax* has been the preferred wax for application to or combining with the sugar.

Wax Coating for Chocolates. Care must be taken in the storage of chocolate to avoid an external condition of a high degree of humidity or too high a room temperature. If chocolate is stored in a damp place, moisture will condense on it and dissolve some of the sugar in the mixture; on later evaporation of the water, the sugar crystals will appear as a "gray bloom" on the surface of the chocolate. Proper working of the chocolate so as to keep the cacao fat well distributed, together with good tempering will tend to prevent the sugar bloom, and so will the addition of a stabilizer such as lecithin to the mix. When the storage room is too warm, the cacao butter in the mass will melt and expand, and the less dense fat will rise to the surface of the chocolate and when chilled, result in a greasy film known as "fat bloom." The fat bloom is not so apt to occur with well conched chocolate. This difficulty in keeping chocolate, particularly the grades produced by the mechanical dippers known as *enrobers*, has led to treatment of the enrobed chocolate with a very thin protective coating consisting of a thin alcoholic solution of shellac, or of benzoin, or a mixture of both. The coating can be applied by spray. *Carnauba wax* however is being used for the same purpose where a luster is desired. Confections coated with wax keep well, do not mold, and preserve their appearance and flavor.

The sapogenin waxes of fruit skins, when freed from saponifiable matter by treatment with sodium hydroxide have been suggested for moisture proofing confections, particularly since they are non-toxic and tasteless as well as emulsifiable.

Waxing Fruits and Vegetables for Market

The processing of fresh fruits and vegetables commercially in preparation for market, has according to Sharma[112] two general purposes: the first of these is to see that the fruit is clean; the second is to do whatever possible to retard the withering or shrinkage of the fruit, so that it will be in as fresh a condition as possible when delivered to the ultimate consumer. Many farm products, as citrus fruits, apples, potatoes and the like, are more or less dirty when harvested. In order to clean these, they are put through a washing process. Nature provides most fruits and vegetables with a natural waxy coating to protect them from drying up and withering. The washing process tends to impair this natural coating and it has been found that the shrinkage rate for these products can be greatly reduced, after they have been washed, by the addition thereto of relatively small amounts of a preservative coating material such as *paraffin wax.*

There are various ways of applying wax to fresh fruits and vegetables. One is by conveying them mechanically through a bath containing the wax dispersed in an aqueous solution, which will be described later on. In another method, recently advanced by Sharma,[112] the wax is dissolved in a highly volatile solvent, and the solution sprayed onto the fruits and vegetables in small quantities to avoid dripping; the solvent is allowed to evaporate without brushing.

Cold injury to grapefruit stored for five weeks at 39° F has been effectively reduced by coating the fruit with an emulsion of *paraffin wax.* Waxing materially reduces the percentage of wilt and loss of weight of apples given any preripening treatment.

Processing with Wax Emulsions. The use of wax emulsions has been generally recognized by growers and shippers as the most effective method of preventing desiccation and improving the appearance of fruits and vegetables. Perishables such as citrus fruits, apples, pears, melons, turnips, carrots, sweet potatoes, cucumbers, squash, potatoes, tomatoes, egg plants, are treated with wax emulsions in suitable equipment, before being packed for shipment.

The equipment generally consists of a waxing-tank, say 10 ft long and 2 ft wide, of 12 gauge steel, and skidded on steel channel irons so that it can be easily moved by placing wooden rolls under the skids. The waxing-tank has a sloping bottom so that a minimum of waxing emulsion is required at the lower end, in which the fruit or vegetable to be treated is immersed. The tank has a conveyor belt which conveys the produce through the emulsion and into the dryer. When using a tank of the size described, 100 to 120 gallons of emulsion are sufficient to give ample coverage over the lower end of the conveyor belt.

The conveyor belt is of sufficient length to permit draining the waxed product before it reaches the dryer. The belt is made of steel wire and carries light wooden slats that will move any type of produce. The dryer is equipped with a wooden roll conveyor belt which is designed to turn the waxed produce slowly as it passes through the dryer. The dryer is about 3 feet wide and 16 feet long, and is open at the bottom. It also has slides in the sides so that the air, picking up moisture from the fruits and vegetables, is allowed to pass quickly out of the dryer. In the top of the dryer of the Korb-Pettit Wire Fabrics and Iron Works, Philadelphia, over the conveyor belt, are located four 22-inch propellor-type fans. To insure perfect and quicker drying on humid days there are twelve 500-watt electric heating units located under each fan. The oven is equipped with an adjustable discharge plate.

Wax-and-Water Spray Emulsions. Apples, pears, and citrus fruits are waxed by means of a spray treatment with emulsions formulated from waxes and emulsifying agents and water. For coating citrus fruits, cantaloupes, apricots, or tomatoes, Sharma[111] employed an emulsion of the following composition: sodium hydroxide 6, triethanolamine 20, stearic acid 42, *paraffin wax* 165, *carnauba wax* 55, shellac 100, and water 2000 parts. This composition is further diluted for use. The spraying of fruit with waxy emulsions in which an amine soap is used as an active emulsifying agent has also been advocated by Cothran,[31] of Pomona, California. Providing fresh fruit with a waxy coating of this character, while it is packed for shipment from the producing sections, has now become standard practice with a large proportion of commercial fruit packers and shippers. The surface of the fruit must not be sealed so completely as to interfere with its so-called "breathing."

The dry method previously in general use, involved the atomization of molten paraffin containing a little carnauba wax into contact with the fruit in a chamber heated to 180–220° F, wherein the fruit was briskly rubbed with horsehair brushes to spread the small quantity of molten wax deposited on the entire surface of each fruit. This treatment cut down the rate of withering by 30 to 40 per cent. The wax emulsion process is much simpler. The wax emulsion may be made up with *paraffin* and *carnauba wax*. A soap of triethanolamine and stearic acid is used as the emulsifying agent to disperse the waxes. The desirable amount of waxes in the emulsion is 4 to 5 per cent. A little pure white mineral oil in the proportion of 1 part of free oil to 5 parts of the waxes is said to give a more continuous coat of wax to the fruit, and permits the use of a thinner film.

Emulsions may be prepared from *paraffin wax* 5, white mineral oil 2½, emulsified with stearic acid 5, triethanolamine 2½, and water 85 parts. A heavier emulsion may be prepared from *paraffin* 7½, white mineral oil 1, oleic acid 1, triethanolamine 1, and water 89½ parts. Oranges, lemons, grapefruits, tangerines, melons, avocados, tomatoes, limes, bananas, etc., all satisfactorily respond to the wax emulsion preservative treatment. Brushing or rubbing of the fruit to finish the protective coating is not required, although sometimes it may be desirable. Benefits from waxing are greatest on fruits having a thin cuticle with the possible exception of the apricot. Waxing reduces water loss but does not overcome decay.

Wax-and-Solvent Spray Method. The use of a solution of wax in a volatile solvent by spray application has been described by Sharma[112] as having distinct advantages, *i.e.*, (*a*) the wax is easy to apply; (*b*) it may be applied without damaging the fruit or vegetables in any way; (*c*) the solvent dries quickly, thus rapidly incorporating the applied wax with the natural protective coating of the fruit; (*d*) the process is economical in the use of applied wax; and (*e*) this process permits a shrinkage control, and regulation in the amount of wax so as to provide adequate respiration of the fruit while it is en route to market. The content of wax in the spray solution is fixed at 7 per cent, and a wax with a minimum cloud point of 34° F is specified. For example, one may use 3 per cent *coconut fat* plus 4 per cent *paraffin*, or 3 per cent *spermaceti* plus 4 per cent *paraffin* in the spray emulsion. The wax-and-spray process has been used in California for citrus fruits to a limited extent.

Waxing of Vegetables. The coating of tomatoes with wax is being successfully accomplished by the use of wax emulsion prepared from suitable waxes, emulsifying agents, and water, as referred to in the Sharma patent for waxing fruits. The waxes usually comprise *paraffin* and *carnauba*. *Ceresin, ozocerite, japan,* with the harder waxes such as *candelilla* and *montan* have been suggested.

For the overwinter storage of sugar beets used in the planting, the mother beets when coated with paraffin and stored show no material decrease in the sucrose content; although the coating reduces respiration it does not cause deterioration. It is desirable to apply the paraffin coating at low temperatures to prevent loss of moisture, and remove it at planting time.

Striking differences are brought about by wax treatment of greenhouse cucumbers stored during three weeks in an ordinary room in midsummer, reducing the weight loss and spoilage.

Wax Colorings for Fruits. In preparing light colored fresh citrus fruit for the market it is desirable to not only retard the withering or shriveling, but to produce a glossy or shiny surface to the ring of a desirable color. Cothran[31a] found that improvements could be made in the commercial grading of lemons by the application of a properly colored wax material to the surface of the fresh fruit. A glossy surface to the lemon is generally preferred to a dull surface, and also a so-called "true lemon-yellow" color.

In some cases the coating is applied to the lemons only just before the final grading and shipment; in others, it is applied also prior to storing or curing them. The lemons brought in from the groves may be thoroughly cleansed with a warm borax solution, rinsed with cold water, and dried; or otherwise cleaned. By then properly applying a very thin coating of suitable waxy material, it has long been feasible to offset the shrinkage. The wax commonly used is *paraffin*, or paraffin admixed with white mineral oil. This treatment imparted too deep a color to the lemon, so Cothran proposed a tint to the glossy transparent waxy coating within the blue-green range. Typical dyes suitable for use are various oil-soluble greens referred to in the patent specifications. These dyes constitute but a fraction of one per cent by weight of the waxy material used for the protective coating. Ordinarily 1 part of dye to 2500 or 3500 of wax may be used, and is sufficient to correct the color to a desirable shade of "lemon-yellow." Cothran claims that where the molten wax material atomized or fogged upon the lemons, as they pass over the polisher brushes, a suitable composition consists of 99 parts *paraffin* and 1 part *carnauba wax*. With no accompanying non-volatile oil, a higher polish is obtainable, which may be further improved by increasing the proportion of carnauba. The slightly amber tint of the carnauba can be offset by a little additional dye in the wax composition. The same principle is applicable to the emulsion spray process of treating fruits.

Waxing of Tobacco. Harsh tobacco may be rendered mild by treating it with a wax emulsion, to preserve the moisture. The matured leaves of the green tobacco plant are normally prepared for consumption by curing, that is by exposing the leaves to air, sun or fire. The cured leaves are then allowed to absorb moisture until they become pliant. The tobacco leaves are then assorted and packed in boxes, hogsheads, or bulks, where the tobacco undergoes a slow fermentation that develops the aroma and flavor. Afterwards the tobacco is worked up in the various forms suitable for the market. When overly-dry tobacco is ignited, irritant products to the smoker's throat and nose are formed, which may be offset by providing an adequate moisture content. According to Andrews[5] this loss of moisture can be checked, and a harsh tobacco made to lose its irritating properties by treatment with wax, and as a resultant effect the tobacco becomes mild when smoked in any form.

The emulsification of the *paraffin* or other wax in water, for the tobacco treatment, is brought about with the aid of an emulsifying agent, *e.g.*, stearic acid with triethanolamine, or simply diglycolstearate. Andrews[6] states that it may be desirable to oxidize the impurities out of the emulsion, if any, by means of potassium permanganate, before applying the emulsion to the tobacco. In making cigarettes it is not necessary to treat the whole blend, but to treat only the "harsher" tobacco constituent. A typical admixture of waxes and emulsifying agent is given as: *carnauba wax* 8, *paraffin wax* 17, stearic acid 2, triethanolamine 0.9, and water 120 parts.

WAX IN THE LEATHER AND RUBBER INDUSTRIES

Wax is used in many different ways in the leather and rubber manufactories. In the industrial application of seasoning to leather by mechanical brushing, wax is used as a base for the brushing compound. For this purpose *carnauba wax, ouricuri wax,* or a *carnauba replacement wax* is used. Soft brush-polish finishes are prepared with the aid of *japan wax,* or so-called *japan replacement wax,* or by means of emulsifiable material having wax in its composition. Wax is often a constituent in leather preservatives, or is the foundation of various kinds of leather polishes and dressings. Solid wax dressings are also used for rubber belting. Wax is the polishing constituent of saddle soap so commonly used to clean, polish and preserve leather goods.

Perhaps the most important function of wax in rubber manufacture is that of an ingredient—to the extent of one per cent—in rubber mixes to prevent sun-cracking of vulcanized goods. The wax blooms to the surface on rubber after vulcanization, and, if in quantity exceeding one per cent, it will give the finished object a gloss and waxy feel. Wax is also used to a limited extent in rubber latices. Natural as well as the hydrocarbon waxes are used in shoe stiffeners.

In the synthetic rubber resins, such as Buna S, *stearic acid* is used as a softening agent in preparation of the commercial crepe. It is possible to mill relatively large amounts of wax with crepe when using preheated rolls. Equal parts of wax and butyl rubber can be mixed in a Banbury or similar type of mixer, to obtain a product of the consistency of gum chicle, and this product may be calendered if desired. Wax is often used in chewing gum to the extent of about five per cent of the composition. The general uses of wax in rubber technology will be described later.

Wax Seasoning for Leather. Seasoning materials are usually applied to leather by hand with a swab, a thin 4 in × 12 in block of wood with plush having a strap across the back under which the hand is slipped. Seasoning machines are also in general use. From one to five coats of the seasonings are applied, each coat being allowed to dry before the next is applied. The concentration of the seasoning materials used, such as egg albumen, is ½ lb or less per gallon. If a brilliant luster is desired, the leather must be glazed. Glazing is done by a 2½-inch diameter cylinder which is moved rapidly across the surface of the leather under high pressure. The heat generated by the friction causes the seasoning to take on a high luster.

Seasonings containing waxes in considerable proportion are not glazed because of the frictional heat which would streak the wax. This type of wax seasoning is usually brushed to produce the luster. The brushing machine carries a revolving brush which will give a high polish to the leather drawn through the machine. *Carnauba wax* can be dispersed in water with casein for seasoning. For pigment finishes stock solutions are made up of one pound to the gallon.

Carnauba, or *candelilla wax*, and *beeswax* are dispersed in soap solution for leather finishes. Waxes are used for their relative softness and tendency to maintain the "leathery feel" as well as to provide luster when the finish cannot be glazed.

According to Davidsohn[33] a soft brush-polished finish suitable for application to shoe calf is obtained from an emulsion prepared from *beeswax* 5, *carnauba wax* 1, olive oil soap 5, ammonia 1, glycerin 1, and water 100 parts. The soap is dissolved in 50 parts of hot water and the ammonia added. The waxes are melted separately and added with stirring to the soap solution maintained at about 90°. The remainder of the water is then added to the properly prepared emulsion together with the glycerin.

Leather Preservatives. In the industry the purpose of a leather preserving oil or wax is to retain the natural grease or oil of the leather, to waterproof the leather against rain, snow and sleet, and if the preservative is applied to shoes or boots, to keep the feet warm. Marine oils are used as preservatives, as are also mixtures of fish liver oil and castor oil. A suitable soft product can be prepared from *wool fat* 2, *scale wax* 3, and mixed fish and castor oils, 6 parts. Tallow and colophony may be used to modify the composition so as to harden it up to the desired paste consistency. *Ceresin wax*, *Utahwax*, and the *microcrystalline petroleum waxes* find an important use in this art. The *crude black montan waxes* used for black leathers are being replaced by somewhat similar black microcrystalline waxes refined from petroleum.

Shoemaker's sewing wax used on thread for sewing leather consists of a composition, more or less, of the following order: *candelilla wax* 3, colophony 54, burgundy pitch 20, rosin oil 4, lard 3, and heavy mineral oil 1 part.

Leather Dressings. The object of a leather dressing is to prepare and preserve the finish of leather goods. The formulation of the dressing is quite dependent upon the use to which the dressing is put, there being no all-purpose dressings. Leather dressings are conveniently classified as to their consistency. They are prepared in three forms: (*a*) liquid, (*b*) solid paste, or (*c*) powder.

The best known leather dressing and the one most widely used is saddle soap. There are inumerable brands of saddle soap on the market.

The consistency of a saddle soap is that of a solid paste, and it is usually applied to the leather by means of a damp sponge or cloth in such a way as to clean the leather, after which the leather can be easily rubbed to a polish with dry flannel or other suitable means. An unpublished formula of Lidard is *beeswax* 50, *carnauba wax* 15, trisodium phosphate 5, castile soap 25, water 120, turpentine 25 parts. Oil-soluble yellow is added in minute amount. In preparing the dressing the waxes are first melted and the trisodium phosphate in half of the water is added to the melted waxes at a temperature of about 190° F very gradually, and with considerable stirring to permit the waxes to emulsify. Then the castile soap dissolved in the other half of the water is added with stirring. Finally the turpentine is added and the whole poured hot into the jars.

A leather dressing prepared by Sajak[105] for miscellaneous uses consists of a mixture of waxes, such as *beeswax* and *spermaceti*, in sperm oil and castor oil. The product is of the consistency of a paste. A product known as Stack's belt-dressing is prepared from rosin 61, *beeswax* 8, linseed oil 7, heavy grease 7, pumice stone 16, and oil-soluble color 1 part.

For dressing finished suede and chamois leather after cleaning, a preparation of liquid petrolatum, or white mineral oil, diluted with suitable solvents, inclusive of high-boiling naphtha, can be used. French polishing powder for leather may be prepared by melting together *carnauba wax* 60, colophony 30, and *paraffin wax* 10 parts. When the melt has become chilled it is finely pulverized, and packaged for use.

Razor strop dressing is made by intimately intermixing an abrasive powder and a mineral lubricant powder with melted waxes into a solid which can be molded in stick form. Kazda[71] prepared a razor strop dressing from pulverized carborundum 5, *paraffin wax* 75, *beeswax* 10, and graphite 10 parts.

Leather Polishes. In the preparation of a paste polish for application to leather goods, it is desirable to use a wax of high-turpentine adsorption value, and which at the same time, produces a high gloss by rubbing after the polish has been applied. An example is the polish proposed by Langenhagen,[76] of Leipzig, Saxony, which is prepared from *carnauba wax* 40, steatite 1, oil of turpentine 30, aniline color 5, Congo black 2, almond-kernel oil 8, *beeswax* 4, and *ozocerite* 10 parts. Leather is known to absorb this type of polish very readily and the gloss resulting from its application to leather is well preserved.

Hydrocarbon Waxes in Rubber Articles. Materials designated commercially as softeners are used in mixes prepared from natural rubber for the purpose of processing on the mill, in the tubing machine, etc. There are numerous softeners such as glycerides, oils, resins, tar, etc., and in this field *paraffin*, and the higher fatty acids as *stearic*, play an important and special role. In the finished rubber product the paraffin hydrocarbons behave as stiffeners, and produce a protective bloom against sun-cracking. Both *crude scale* and *refined paraffin wax* are used in molded goods, hose, and jar rings. Solid tires such as those used on baby carriages are sun-proofed with paraffin wax. The wax is added directly to the rubber in the Banbury mixer. *Ceresin,* like paraffin, has the peculiar property of working toward the surface of a rubber article, much in the same manner as sulfur blooms. The degree of blooming does not necessarily depend upon the quantity of wax used, and is greatly influenced by the general make-up of the rubber mix as to the percentage of fillers, etc. As little as one per cent of paraffin wax in the rubber will make it proof against sun-cracking. Paraffin is used in rubber auto-topping and miscellaneous tubing of various kinds, *e.g.*, windshield wiper tubing, and in rubber flooring compositions.

Paraffin wax is often used in rubber to a greater extent than is simply needed to prevent sun-cracking, particularly where mechanical rubbers require a low friction surface, and may be used up to 5 per cent of the weight of the rubber, although pronounced blooming occurs in excess of 3 per cent. Paraffin used in this manner produces a non-staining surface. *Paraffin wax,* or *stearic acid,* is used as protective substance on colored rubber to prevent it from decolorizing. Fatty colors of the lipoid type are intermixed with rubber and waxes of fatty acids, the latter preventing the penetration of the dye to the outer surface of the article.

Commercial Agents for Retarding Deterioration of Rubber. The use of paraffin wax to prevent the sun-cracking of rubber has already been referred to. Davis and Blake[34] mention several types of hydrocarbons, or hydrocarbon-containing waxes, used in retarding deterioration of rubber. These have trade names such as "Heliozone," "Sunproof," and "Agerite Gel." They state that waxes are of value solely for protection against deterioration by light or ozone. This is perhaps somewhat at variance with the generally accepted opinion. In the commercial agents we may have a combination of an antioxidant with the wax, which greatly intensifies the protective action of the latter. It is believed that the wax blooms out in a form saturated with the antioxidant, from the vulcanized rubber, and furnishes the best known protection against chalking and sun-checking. The waxes most commonly used to obtain resistance to light and ozone, and rid the rubber articles from checking—that is developing small cracks—under "corona effect," are *paraffin wax, ceresin wax* and *ozocerite.*

The wax is used to the extent of a half to two per cent, based upon the rubber content, for articles that are exposed near high-tension wires and electrical discharges. The severe cracking that is experienced with many forms of electrical rubber goods by the higher concentrations of ozone has become a baffling problem. A high proportion of a waxy ingredient in wire and cable insulation, and electricians' gloves is helpful in this respect.

Wax in Latex Rubbers. It is often necessary to add a softening agent to a latex rubber in order to overcome its excessive toughness, and the commonly used softeners for the purpose are *stearic acid,* mineral oil, and *paraffin wax.* *Stearic acid* when so used, is added to the extent of 2 per cent or more, on the basis of the weight of the rubber. The addition of stearic acid is effected through the preparation of an emulsion which is intimately mixed with the latex. To prepare the emulsion, 4 parts of stearic acid are melted with 1 part of oleic acid, and this melt is vigorously stirred into 5 parts of a potassium hydroxide solution of 0.12 per cent strength, after which 0.3 part of stronger ammonia solution is added with continuous stirring. The emulsification is best carried out at a temperature of 70 to 80°.

In the production of colored rubber articles from latex by the dipping method, free stearic acid is used in conjunction with latex dispersions, by dissolving the stearic acid in a suitable organic solvent in which one per cent of the fatty coloring material is intermixed. A waterproof composition for proofing paper, fabric, etc. is made by intermixing an emulsion of a hard wax with latex.

Fully refined hydrocarbon waxes may be used to coat an aircraft covering that has been previously prepared by coating a fabric, under tension in stretching frames, with a rubber cement followed by certain latex coatings. The wax is of value as a sun-proofing agent for the rubber surfaces. The art of preparing the aircraft covering is taught by Calvert in his U.S. patents.[20]

Paraffin of a hard quality or *spermaceti* is used for coating synthetic violin strings just prior to application of the finishing coat of soapstone or luster varnish. The strings of silk, wool, hemp, or other suitable cord material will have been impregnated with rubber latex, imitating strings of catgut, before coating with the wax.

Belt Dressings. Belt dressings for use on heavy duty belts made of rubber or other materials should provide oil for the belt and a tacky substance for traction. A belt treated with a dressing of the kind described will have an extended life, and there will be less strain on pulley bearings than if the traction were obtained by tightening alone. The two principal types of belt dressing are the "liquid type" and the more popular "stick type." A disadvantage in using the solid kind is that it imparts but little oil to the belt, the stick being prepared with colophony and wax, with but a small amount of oily ingredient. Waxes, unless properly chosen, tend to lessen traction. The great advantage of the stick lies in its ease of application to the belt.

The liquid type of belt dressing is prepared from a combination of two or more of the following classes of oils: mineral, marine, animal, and vegetable. With the oils are mixed a small amount of oleo-resin (perhaps a combination of colophony and pine tar), and a perfume oil such as oil of mirbane.

In a belt dressing of the solid type, that is the sticky dressing, waxes are ordinarily used in the composition. The waxes commonly used for the purpose are *beeswax, montan wax, wool wax,* and *scale wax.* In some formulations *stearine* is used, together with the wax, rosin, and a viscous oil such as castor oil. A tacky wax such as *petrolatum wax* may also be used to advantage in stick dressings.

Shoe Stiffener. In the manufacture of shoes heated machines, employing metal or other rolls, burnish heels and bottoms distributing a film of wax over the surface. In the making of the box toes it has been customary to use a stiffener between the upper and the lining of a shoe and put the shoe in a heater to which moist heat is supplied. The stiffener is thus rendered limp and plastic, and the operator then inserts the prepared shoe in the pulling-over machine to carry out the pulling-over operation. Somewhat similar treatment follows at the toe-laster. The shoe stiffener when cooled must become hard, and rigid in the shape of the last, and hold its shape indefinitely. *Montan wax* formerly found an extensive use in this art in the United States, but has now given way to various substitutes, including the synthetic waxes. According to Swett[119] a fabric material for box toes or shoe stiffening can be well prepared by impregnating the fabric with a rubber, wax, and resin composition. A varied group of waxes are said to to be suited to the purpose, *e.g., carnauba wax, beeswax, shellac wax,* or the *microcrystalline hydrocarbon waxes.* The wax selected is then blended with a paracoumarone or coumarone-indene resin, and melted with rubber to produce the stiffener. Swett gives the following recipe: Nuba resin 45, colophony 30, rubber reclaim 15, and *candelilla wax* 10 parts. The ingredients are weighed out in a common vessel, heated to about 370° F and simultaneously agitated. The result is stated to be a homogeneous, molten, water-free, impregnant of a viscosity suitable for the saturation of a wide range of bibulous fabrics or fibrous bases such as felt, paper, textiles, and the like. Upon cooling the stiffener has the property of being thermoplastic when warmed, but rigid when cold, yet retaining elasticity.

Tailors' Dummies. Molded forms such as tailors' dummies for window display can be made by applying to a textile base a molten composition of *vegetable wax,* rubber, *beeswax,* and resin; and then forming the resultant thermoplastic material by means of steam heat to the desired shape and form. The textile base used for treatment with the impregnating compound, is preferably a double ply, or multiple ply, knitted fabric so that the compound may deposit in the plies, between the plies and as a surface coating on the plies. When the coated textile base material is steam heated it becomes limp, adhesive and tacky, and can be made to conform accurately to the contour of the model. Dress forms from a human model provided with a close fitting garment can be made. The composition is said to be more durable than plaster of Paris, or papier maché and gummed tape, for the purpose. Lovell[82] has given the preferred recipe for the coating composition as: *Candelilla wax* 30, rubber 10, *beeswax* 10, resin or colophony 50 parts. The rubber is melted with the resin, and the rubber-candelilla mixture dissolved in molten beeswax-resin solution, at about 320° F with thorough stirring.

Chewing Gum Base. Gum chicle, a selected balata, pontianak rubber, gum gutta, and similar rubber related material find their way into the manufacture of chewing gum. Generally speaking these rubber like crudes must be broken down by milling before they can be made masticable. For example, when chewing gum is made from crude pontianak rubber it is necessary to kneed the rubber at 93 to 149° until its resiliency is destroyed; a little water is added together with the sweetening and flavoring ingredients, and about five per cent of a vegetable wax, such as *candelilla wax.* The pontianak resins, purified by treatment with alkali and sugar solution, and with super-heated steam, may have coconut oil, *vegetable wax, paraffin wax, japan wax,* or other waxy material incorporated in addition to the usual flavoring and sweetening ingredients. Carmody[21] proposed combining a synthetic resin with rubber, of the chewing gum kind, vegetable oil and wax, making the synthetic resin the predominating masticable ingredient. Carmody's chewing gum can be made from hydrogenated pinene resin 66, chewing gum rubber 25, vegetable oil 5, and wax 4 parts. *Candelilla* is the preferred wax, but other waxes such as *beeswax* may de used. To complete the chewing gum, twenty to twenty-five per cent of sugar is added together with suitable flavoring material. The gum is dusted with powdered sugar in the conventional manner. The composition lends itself to producing stick, ball, tablet or other forms.

WAXES IN LUBRICANTS AND SKI WAX

Wax as a Lubricant. There are several ways in which waxes are used as lubricants: (*a*) in a solid cake or stick form, (*b*) in mist or powdered form. (*c*) in a slushing compound, (*d*) in a water emulsion.

(*a*) Small objects may be lubricated by tumbling them with rough chunks broken from a solid cake of a hard wax, in a barrel rotated at a slow speed for a period of time. When the objects are removed they will have a slight coating of wax and a greasy feel. Cork discs for bottle caps have been treated in this manner.

Lubricating wax is used where oil or grease do not serve the purpose well. A stick form is used in the automotive trade on the dovetails and lock tongues of automobile doors, and also on the hood lacings to prevent squeaks, rattles and wear. A stick composition prepared by Rosen[104] is made by mixing together petroleum jelly 18, oil 18, mica 5, and waxes 59 parts. Waxes suitable for the purpose are *ozocerite*, *carnauba*, *petroleum ceresin*,, *paraffin*, and the like. In preparing the stick the wax is melted and the oil added, also the finely divided mica; the entire mixture is raised to a temperature of 250° F and agitated; then allowed to cool to 160° F before it is poured into the molds. The stick is hard and brittle but will become plastic and lubricate when pressure is applied.

(*b*) Paraffin can be used to lubricate objects by placing them in an oven where they are sprayed with molten *paraffin wax* in the form of a mist. The plan is to spread a solid lubricant in a continuous film on the object which may be cardboard, molded plastic, metal, etc. Paraffin, ceresin, or other waxes are used in spray machines designed to pick up the molten wax from a small heated fountain and deliver the wax to the printed sheets of paper or metal in a very finely divided droplet condition before the sheets are stacked, in order to keep them apart and avoid smudging. This process is known as Grammer Spraying. Metal sheets with lithographed designs can be sprayed by such a process and fabricated into bottle caps without injury to the design.

(*c*) Petroleum waxes make suitable lubricants for a deep drawn metal stamping. The wax is melted and a sufficient amount of high boiling naphtha added to form a slushing material on cooling. This mixture is then applied to the metal sheet in a thin layer by a felt swab, or rollers before the sheet is stamped. This method has more or less replaced a method where the felt swab was first dipped in benzine and then rubbed over a solid cake of wax before stamping the sheet of tin plate or black plate.

(*d*) An example of water emulsion suitable for lubrication may be prepared according to the following formulation: water 90.7, triethanolamine 0.67, *scale wax* 22.7, and stearic acid 2.35 parts by weight. The water and triethanolamine are heated together at 72°. The scale wax and stearic acid are also heated to 72°, and then the two mixes are combined, and agitated until cooled to room temperature. This water emulsion may be applied to sheet metal by swab or felt roll to lubricate it for fabricating cans, toys, pans, etc.

Ski Wax. The ski or wooden snow-shoe requires repeated treatment of its running surface so that it will glide easily in downhill progression and avoid back slippage in uphill progression. The Norwegians first apply a foundation of pine-tar, and then wax hard, especially at the tip. The greatest use of ski waxes is for the military both in America and on the European continent. Three kinds of wax are chosen for the American army, and these are distinguished in use by colored labels—blue, red, and orange. These waxes are "dry snow wax" for very cold temperatures, "medium wax" for temperatures near freezing point, and "wet snow wax."

Before waxing, the running surface of the ski should have several layers of a good quick-drying lacquer, which can be applied with a soft brush; *e.g.*, a liquid ski dressing according to Flint[45] is formed of celluloid $\frac{1}{2}$ oz., acetone $\frac{1}{3}$ pint, shellac $\frac{1}{6}$ pint and powdered graphite $\frac{1}{12}$ oz. Waxing helps the ski to glide easily over the snow crystals; the drier the snow the less wax, and the wetter the snow the more paraffin needed. *Paraffin* prevents lumps of snow from forming on the bottom of the ski better than any of the stickier types of waxes. Harper[56] states that paraffin is an especially fast wax on new or melting snow; it wears off quickly and must be applied very thickly.

Harper states that below zero "Red Wax" can be used in a thin layer; and applied medium thick with a little paraffin above zero; and above 32°F the "Red Wax" applied thick with a thick layer of paraffin. On iced, crusty, or granular snow it is advisable to use several layers of wax, *e.g.* "Red Sohm Wax," and paraffin, because these types of snow wear off the wax very quickly. A "Blue Wax" may comprise $\frac{2}{3}$ wood tar and $\frac{1}{3}$ hard waxes; a "Red Wax" $\frac{1}{2}$ wood tar and softer waxes; and "Orange Wax" little or no wood tar, but rosin, and softer waxes. There is a considerable variation in the kinds of waxes selected for the makeup of the various commercial brands.

Wax is put on the ski with the palm of the hand or with a cork. A flatiron does not allow the wax to penetrate the ski sufficiently and should not be used. According to Harper a torch is the best device for applying wax to skis. It is also handier to depend upon one wax, such as Red Wax, than to use three different waxes to suit snow conditions.

For cross-country skiing it is advisable to apply to the skis a foundation of tar or "Klister" instead of the lacquer foundation. The application is hot by means of a torch, and the foundation keeps the skis from sliding backward on the upgrade. When the snow is wet the cross-country runner may mix the wax with "Klister" instead of paraffin. A preparation of this sort is given in a recent Russian patent.[10] This wax is prepared by mixing rosin tar, turpentine, ozocerite, heavy mineral oil and the sodium salt of rosin acids.

In using the U.S. Army waxes a thin layer of the Wet Snow Wax is applied over the Dry Snow Wax (Orange over Blue) for climbing purposes at sub-zero temperatures.

When using the Wet Snow Wax if there is a tendency of snow to stick to the wax, some Speed Wax is rubbed over it (Red over Orange). The Speed Wax is however, not suited to climbing. American waxes are compounded from *microcrystalline wax, paraffin wax, beeswax,* and other suitable waxes. For fast running the stickier wax constituents which are valuable for climbing must be reduced to a minimum.

The U.S Quartermaster Corps, Tentative Specifications (B Q D No. 85) for Ski Wax covers three grades known as E-1, E-2, and E-3. The E-1 calls for Orange, for Wet and Corn Snow, Climbing and Running Wax; E-2 calls for Blue—Climbing and Running Wax (of different characteristics from E-1); E-3 calls for Red, Speed Wax—Running Wax for Sticky Snow Conditions.

The E-1 or Orange Wax is for climbing and running in dry snow at sub-zero temperatures. The wax must allow easy gliding in wet snow or corn snow; must allow climbing without back-slipping in corn snow, and in powder snow at sub-zero °F temperatures on a slope of at least 18 degrees. It must rub to running surface easily and rub out to an even layer with the palm of the hand or a cork at temperatures down to 32° F. The wax must wear at least as well in wet or corn snow as leading brands of "Klister." It must not emulsify. The wax must have a nearly white or transparent color, it must easily push up and down in tubes, and must not deteriorate in storage.

The E-2 or Blue Wax must allow easy gliding over all types of snow. It must allow climbing without back-slipping in powdered snow at temperatures between zero and 30° F on a slope of at least 15 degrees. It must apply easily outdoors as well as indoors and form an even surface without lumps when rubbed to the running surface. It must have good adherence to lacquered ski bottoms and wear well in any type of powder snow; an application should at least wear for a 10 mile ski run. It is expected that the color will not be darker than ivory, and that the wax will contain not less than 20 per cent of beeswax by weight.

The E-3 is designed for fast running in all kinds of snow. It must apply easily outdoors and form a smooth surface when applied over wet or dry snow climbing wax or over a lacquered ski bottom. It must wear at least twice as long as plain paraffin. It must be of a white or nearly white color, and shall not contain less than 8 per cent of beeswax by weight.

WAXES AS ANTIOXIDANTS AND POUR POINT DEPRESSANTS

Wax as an Antioxidant

Machinery, or machine parts, must often be protected from rust, particularly so when they are exposed to rain, snow or sleet. They must be protected in overseas shipment through extreme changes in temperature and relative humidity. For this purpose an antirust composition which contains wax may be used as a surface coating for the metal. A composition which cannot be easily removed by ordinary abrasion but which can be washed off later with gasoline is to be preferred.

Wax is also used as an ingredient in certain antioxidants employed for doctoring motor oils in preventing carbonized sludge from forming.

Slushing Oils. Slushing oils of a prescribed composition are used as protective coatings for exposed bright metals, or polished surfaces, to keep them from corroding. The specifications for a slushing oil have been given by Walker and Steele[125] as follows: The material shall firmly adhere to all metal surfaces at all temperatures to be met with under natural conditions and shall permanently remain in such condition that it may be readily removed by cotton waste wet with kerosene. On polished steel, iron, brass and copper surfaces at any temperature below 100 for not less than 5 days there shall be no stains or other evidence of corrosion. An oven salt-spray rain test is also specified and when time permits plates covered with the material should be exposed to weather test for 60 days with no appreciable rust in evidence as a result. Slushing oil leaves a soft film which can be easily removed at any time. Typical formulas are (*A*) *candelilla wax* 3, rosin (grade H) 6, *petrolatum* (U.S.P.) 50 parts; and (*B*) *carnauba wax* 2, rosin (grade H) 5, and *petrolatum* (U.S.P.) 50 parts.

Another type of antirust composition employs anhydrous lanolin as the wax ingredient. This is the composition of Howe and Libby[61] which is of the following order: petrolatum 32, *anhydrous lanolin* 32, mineral oil 15, and mica flour 18 parts. To this may be added cedar oil 1, and graphite 2 parts, if desired. The purpose of the mineral oil is to thin the composition so that it may be easily applied to polished machinery by brush or otherwise. The lanolin and petrolatum make the coating cling to the metal. The mica makes the composition more compact, increases the coverage, increases resistance to the elements, and prevents the composition from rubbing off. The composition can be removed by using waste moistened with gasoline or kerosene.

✓ **Antioxidant for Lubricating Oil.** For the elimination of carbonized sludge formed by oils operating at a high temperature, *e.g.* 550° F, over a period of time, Joseph Cole[27] of Whiting, Ind., prepared an antioxidant composition with a base of *chlorinated paraffin wax* (43 per cent Cl) to add to the lubricating oil. The antioxidant is a compound of the wax 250, oleic acid 250, and anhydrous aluminum chloride 15 parts, all heated to 550° F, with constant stirring. A reaction takes place in which hydrogen chloride is evolved during heating, whereupon lime (25 parts) is then added and the whole transferred to a still; under 10 mm vacuum, eighty per cent of the product may be taken off on distillation. This distilled product has a gravity of 34 A.P.I., and about 1 per cent is added to the oil.

Wax as a Pour Point Depressant

Polymers of waxy olefins, with or without chemical condensation, with cyclic hydrocarbons, are used as pour point depressants. Wax modifying agents have been made chiefly by aluminum chloride condensation of waxy hydrocarbons with cyclic compounds, such as naphthalene, anthracene, etc. According to Lieber,[81] wax modifying agents can be produced more cheaply by condensation using certain acid condensation substances. It is necessary first to convert chemically the saturated hydrocarbons to olefins (alkanes to alkenes), and polymerize the olefins by means of strong acids, and then recover the wax modifier, all in the manner described below:

In making these latter modifiers by the Lieber process, the wax in molten condition is first halogenated by blowing chlorine through the melt at a temperature from about 150 to 300° F. Various chlorinated compounds result. It is preferable to limit the chlorination to about 10 to 12 per cent in order to produce the optimum wax modifying activity. The chlorinated wax is then dechlorinated, preferably by heating to a high temperature and permitting the hydrogen chloride to split off and escape. By keeping the heating temperature below about 700° F, a mixture of olefins is produced corresponding to the mixture of chlorinated hydrocarbons, without breaking any of the carbon to carbon bonds. The dechlorination at the lower temperatures is facilitated by the presence of catalyst, such as anhydrous barium chloride or activated clay, both of which have the power to split off hydrochloric acid at reduced temperatures.

Polymerization is carried out in a liquid state by stirring for a long period with either sulfuric acid or phosphoric acid, preferably 60 to 66° Bé sulfuric acid, or 85 per cent phosphoric acid. The acid is dropped slowly into the hydrocarbon mixture which is continuously stirred for about an hour. The reaction takes place at 250° F or less, and must be controlled to prevent carbonization. Active depressants can be made from a concentrated acid at 120° F, with a reaction time of one hour, but more potent products are obtained by increasing the reaction time to five hours or more. After the reaction period has elapsed the acid is removed by neutralization with caustic soda, and the hydrocarbon content of the reaction mixture, including the modifier, is taken up in kerosene so that it may be separated from the acid sludge. The final step is to distill off the solvent and recover the wax modifier from the distillation residue.

Wax modifiers can also be made with the addition of cyclic materials such as benzene and toluene, but preferably naphthalene, anthracene, or phenanthrene. It is advisable to use somewhat less than 30 per cent of the weight of the olefins when condensing with the aromatic.

The polymer produced with sulfuric acid from waxy olefins in the absence of aromatics, has an A.P.I. gravity of 22.3, a Saybolt viscosity of 293 at 210° F, and 4262 at 210° F and a pour point of +45° F. When 1 per cent of this material was added to a waxy oil which had an initial pour point of 30° F, it was found by Lieber[81] to be reduced to 5° F; 5 per cent of the same material added to the same oil reduced its pour point to −20° F. In the above example 85 cc of 95 per cent sulfuric acid was added to 800 cc of 95 per cent sulfuric acid. However, if the acid is doubled a depressant can be made so that when 1 per cent thereof is added to the oil, the pour point may be reduced from 30° to −25° F.

WAX IN MATCHES

Historical Aspect. The earliest use of wax in matches appears to have been in an impracticable contrivance known as the phosphoric taper, which dates back to 1781. This was of wax, enclosed in a sealed glass tube, at the end of which was a fragment of phosphorous. After the tube had been dipped in warm water, the end remote from the phosphorous was cut with a file, the taper was withdrawn, with some of the phosphorous adhering to it, and spontaneously inflamed.

The first useful friction match was invented in England by an apothecary, John Walker of Stockton-on-Tees, Durham, in 1827.[36a] The tips were made from a composition of potassium chlorate, sugar and gum arabic. The method of striking to obtain fire was to draw the splinter tipped with the composition over a piece of sandpaper. These so-called "friction-lights," or friction matches, were supplied in tin boxes, together with a piece of folded sandpaper. Imitations of Walker's matches appeared on the London market in 1829 and for a few years thereafter, under the name of "lucifers," but these likewise were difficult to ignite. To increase the inflammability of the stems they were sometimes dipped in hot tallow, resin, and wax, but most of the stems were dipped in sulfur to make them readily inflammable.

In 1832 match boxes were made with special striking surfaces, a development which was also made possible by the improved chemical composition of the tip, namely a mixture of potassium chlorate, antimony sulfide, sulfur, and gum arabic. The strike-on-box matches were sold in England and abroad under the name of "congreves," after Sir William Congreves, inventor of war rockets at that time, and they replaced "lucifers." In 1831, a Frenchman, Dr. Charles Sauria, of St. Lothair replaced the antimony sulfide component of the match tip by phosphorous, thus improving the practicability of the friction match, which became now known as the "phosphoric friction match." In the United States a patent was granted in 1836 to A. D. Phillips for the invention of a "strike-anywhere" match, whose igniting composition was a mixture of yellow phosphorous, sulfur, chalk, and glue. The use of phosphorous sulfide instead of phosphorous was proposed by Puscher, of Nuremberg in 1860. Hannan and Mills of England, in 1882, proposed a friction match paste containing wax and resin.

Fire hazards with phosphorous friction matches led to the preference for a "safety match," in which the inflammable portion of the match head composition, chiefly amorphous phosphorous, was affixed to the side of the box. This early invention of 1844 is generally credited to Pasch of England, even though it was not placed in commercial manufacture until 1855, and then in Sweden by Lundstrom. The Swedish safety matches had the oxidizing mixture on the match heads and red phosphorous on the box. Phosphorous sesquisulfide, which is non-poisonous, was introduced in match manufacturing establishments in Paris in 1898 to replace phosphorous. Its use in the United States quickly followed for "strike-anywhere matches."

The introduction of wax for treating wooden stems, or splints does not seem to have become extensive until 1861, when Letchford of England recommended using melted paraffin, and a mixture of *paraffin* with *stearin*, and *japan wax*, which were regarded as substitutes for sulfur previously used. The use of colored paraffin was proposed by Bell in 1891. Paraffin has now become universal for the coating of match splints.

The use of solutions of fire retardant chemicals for the treatment of wood splints dates back to 1879, and has now become a general practice with the American match manufacturer. A solution of ammonium phosphate with ammonium sulfate is commonly used for the purpose of impregnating the splint; the splint is then dried and paraffined.

Wax Treating Wood Splints. In order to communicate rapidly the flame from a burning match head to the stick it is necessary to treat the splint with a highly inflammable substance, such as sulfur, phosphorous, or wax. The treatment of the wood splint with *paraffin wax* has survived all other methods as being the most practicable one. Match splints, therefore, regularly receive a paraffin treatment prior to the application of the ignitive compound at the end. This method of paraffin treatment is automatic in the modern type of match machine equipment. The splints are placed in a hopper, and by means of a joggling mechanism and plungers, are inserted into the so-called match plates. These match plates have perforated holes, usually in rows two abreast, to receive and carry the matches, and form links of a continuous chain, or endless belt. The chain travels slowly and conveys the splints, tips downward, over a hot plate, and through a steam-heated bath of melted paraffin wax held at a temperature of 220° F. From the paraffin bath, the splints are conveyed over a dipping roller, which revolves in a trough or fountain containing the match-head composition. From the match paste trough the matches pass over a series of large diameter drums or carrier-wheels, where they are dried by currents of air. After having traversed the carrier-wheels, the dry finished matches reach the starting point of the endless chain, where they are ejected by plungers to meet the holes in the match-plates, and are then packaged by suitable box filling equipment. The entire cycle of operation covers an hour's time.

American Manufacture of Matches. In American manufacture of strike-anywhere-matches the procedure is modified somewhat from that described above. Fairburn[44] proposed the treating of match splints to render them combustible, but non-glowing by dipping the splints into a flowing stream of molten paraffin in which boric acid and alum, or other fire retardant is suspended. Customarily the splints are impregnated with ammonium salts for the purpose of preventing a glow of the stem after extinguishing the flame. The splints must be dried before putting them through the paraffin treatment. The preferred wood splint is the round and grooved stick, which after paraffining receives a double dipping; first a dip to give the match the bulb, and a second to form the "striking eye" which is usually a different color. This invention is credited to the Saginaw Match Co. In the double-tip match the striking-eye has the more ignitable composition. Double dipped matches in the process of manufacture are best dried after the first dipping in an atmosphere of 30 per cent humidity or less at 38–65°, and after the second dipping at 50–65 per cent humidity and 20° temperature.

The paraffin wax preferred for paraffining match splints has a melting point of 124–126° F and is relatively free from slack oil. Without the wax treatment the ignitive head would not adhere tightly to the stick. Higher melting paraffins can be used, but prove more costly. The large manufacturers purchase their paraffin in tank car lots and store it in steam heated insulated tanks to keep it in a liquefied condition, so that it can be pumped directly to the match machines as needed. Emphasis is placed on keeping the temperature of the wax bath at 240° F or above to prevent the latter occurrence of a match bulb flying from the stick when the match is struck, which will happen when a wax fails to penetrate the wood splint.

Wax in Match Heads. According to Crass,[32] a number of match manufacturers incorporate a small amount of paraffin wax, that is about 1½ per cent of the total batch volume, in their bulb composition (not the striking-eye) for the match head. The addition of paraffin has the effect of producing a smooth, quiet, burning match, the flame of which is generous and billowy in character. In making such a composition the hot melted wax is added to the hot glue solution before the addition of the other ingredients, and thoroughly mixed in order to get adequate dispersion of the wax in the glue. The prepared composition is velvety and has a dull luster which is carried over and imparted to the finished match head, thereby increasing the attractiveness of its appearance. However, Crass further states that the value of such wax additions is open to question because of their tendency to reduce the bonding efficiency of the glue and to make the match head brittle and more susceptible to crushing and flying, when it is struck. Such matches also tend to soften at elevated temperatures. Resistance to moisture is improved, however, which is of distinct value under certain climatic conditions.

Swedish Matches. Swedish matches are generally recognized as safety matches prepared from wood veneer of poplar, cut by means of a guillotine knife, which causes them to have a square cross-section. The splints of wood are kiln dried and the end to be covered with the ignitive compound is dipped in a solution of paraffin in benzene, whereupon the splints are again dried. They are then dipped in the match head compound which is of such a consistency that only small drops adhere to the splint. The compound is usually made up of potassium chlorate, red and/or yellow lead oxide, antimony trisulfide, potassium chromate, gum arabic, *paraffin wax*, and water. The brown color of Swedish matches may be ascribed to the presence of the antimony. The paraffin is generally rubbed up with the antimony and then incorporated in the compound.

Formulas for the compound are modified in order to secure quick ignition and quick flaming, or retarded flaming, if desired. The striking surface on the box employs no paraffin. It is a compound of amorphous phosphorous, sifted iron pyrites, pulverized glass, and a little gum solution; or a compound of similar character. The most important Swedish match manufactories are those of Jönköping, such as the Vulcan factory at Tidaholm.

Sulfur Matches. Sulfur matches have the ends dipped into melted sulfur, stearic acid, or wax, and then into a compound of potassium chloride, antimony sulfide, and glue water. A sulfur match is of the strike-anywhere type and when ignited has a long-burning match head.

Parlor Matches. Parlor matches are strike-anywhere matches which have a lustrous colored match head. The original Austrian type of "de luxe" or parlor match had the match head treated by hydrogen sulfide which gave it a silver appearance. The use of colored lacquers for coloring the lustrous heads began in 1879. Parlor matches have the sticks soaked in *stearic acid*, and then dipped in the match-head compound of phosphorous, gum, water, fine sand, and red lead; or other suitable composition.

Wax Matches. Matches with wax stems were known in England as "vestas" and date back to 1832. In the same year Siegel, in Vienna, combined resin with wax to produce a firmer match stem. "Vestas" were first produced on a commercial scale in 1836, by Savaresse and Merckel in Paris, who used a composition consisting principally of *stearic acid*. Later, in England, *stearic acid* and gum copal or gum damar proved to be a satisfactory composition for the stems. The use of *carnauba wax* to harden paraffin for the same purpose was proposed by Childs, of England, in 1862. Strips of veneer, with one or more threads applied longitudinally form the case patented in England by Stedman in 1906.

Wax matches are produced from long wax tapers which are then cut off at match lengths. The wax receives its support from strands of cotton, strips of bristol board, twisted paper, threads of jute, or other suitable core material. The wick material is drawn through the wax in a steam-jacketed tank, and thence through perforations in a draw-plate, and afterwards over a drawing drum, then back into the wax tank, and then over an opposite drum, and so on, until these alternate windings produce a sufficient coverage of wax so that the taper can pass through the holes in a suitable gauge plate; finally it passes through a heated perforated plate which polishes the taper. The taper is then cut to the match length by a wax machine of a continuous type (as that of the Diamond Match Co.) which delivers the stems to the dipping roller for application of the match-head compound, and then dries them over carrier wheels.

Book Matches. "Book matches" are of the safety type, striking only upon a prepared surface. They are manufactured by machines which automatically print the cardboard, paraffin it, cut it into combs, dip the teeth in the match head composition, fold up, stitch into books, and affix the striking compound in a strip on the exterior of book. Generally, there are two layers of matches to a book. A series of patents were granted to Criswell, of New York, in 1911, on the making of match splints from paper making pulp, that is by compressing the pulp into long united splints, which are then severed by cutting between the splints, and likewise in a transverse direction for the measured lengths. These paper splints are then coated at the tips with paraffin, and then with the ignitive compound. A paraffined paper pulp stem will produce a billowy flame quite similar to one made of wood.

MOLDING AND CASTING IN WAX

Techniques of Molding and Casting

Molding and casting are processes of reproducing an object in form, and often texture and color, identical in appearance with the original from which the copy or reproduction is made. Molding and casting as a unit is referred to as "moulage," although this term sometimes designates the finished cast or positive.

When reproducing an object such as the human face, the face (after greasing) is covered with a thin layer of wax, by spray or by brush, and over this an outer shell or case of plaster of Paris is built up as a supporting medium for the wax impression of the face. This impression is called the mold or negative. When the mold is removed from the face, it is filled with a suitable substance to make what is known as the cast or positive. If an entire human head is to be molded, two profile molds are made, which are later fitted together.

Materials for Making Molds. Many materials, such as plaster, agar, composition glue, sulfur, rubber, baked sand, terra cotta, etc., are suitable for making molds. Wax however is particularly applicable to molding small or delicate objects such as fruit, flowers, coins, medals, or the hands and face.

Artisans find through experience what appear to be the best waxes or wax compositions for each purpose. For example, rosin 1, *white wax* 3 parts, is suited for casts. However, for molding of the face or hands a wax of a different composition is used. The wax must be tolerated by the skin, and naturally must be one of low melting point. A wax mixture known as B-11 described by Golden,[52] is composed of *paraffin* (m. 51.7°) 55, *bayberry wax* 20, *carnauba wax* 5, and *stearic acid* 20 parts. This mixture has a melting point of 53°, and is sprayed on the greased face, or other object, by means of a De Vilbis type CB spray gun, at a pressure of 4 to 6 pounds. The first layer acts as an insulator for a second layer, about one-half inch thick, which is applied by spatula when the wax is in a congealed state. Small rubber ice bags may serve for chilling the wax. It is customary to support the mold with a sufficient quantity of plaster of Paris.

A wax composition for application with a camel's hair brush instead of a spray is as follows: *bayberry wax* 50, *paraffin* (m. 51.7°) 25, *stearic acid* 25 parts. This mixture has a suitably low melting point, 42.0°.

To cast a plastic positive in a plaster negative it is necessary to use some separating medium between the two. *Yellow beeswax* 1, carbon tetrachloride 9 parts, makes a desirable separator. Paraffin 1 dissolved in benzene 5 parts has also been recommended.

Separating Mediums for Moulage. If the mold is plastic and the cast is a wax composition which is to be removed from the mold, this can be accomplished by soaking the moulage in a sodium or potassium citrate solution. Sometimes potato starch is used with the plaster so as to enable the mold to distintegrate.

To separate wax from plaster, the plaster mold is soaked in warm water before pouring or painting on the wax. It is then soaped with shaving soap or other suitable lathering soap, the excess wiped off with a brush and the mold polished. A thin film of soap facilitates easy separation of the wax positive from the plaster mold.

Clarke[24] states that the best positive material for producing a lifelike reproduction of flesh is a composition having a resin and wax base, and resin-wax compositions are of great value for the casting of medical and biological subjects. Clarke has laid down definite specifications for resin-wax compositions that involve plasticity, melting point, shrinkage, etc.

Positive Impression Compositions. Waxes for positive impression compositions usually comprise suitable mixtures of waxes, mineral clay, and possibly resin, and starch. Starch is of value where water is used to assist removal of the positive from the mold in moulage practice. According to Clarke,[25] positive wax impressions may be prepared by the formula of Douglas, which is *white wax* 4, *paraffin* 3½, talcum 2, cornstarch 2, and *yellow beeswax* ¼ parts; or by the formula of Ziskin, which is *refined paraffin* 22, *pale carnauba wax* 2, *beeswax* 1, and *dark carnauba* ½ parts. Carnauba wax itself has high cohesive and low adhesive properties, but is of value as a hardener and as a "booster" of the melting point of the composition. Clarke found that the introduction of a microcrystalline wax of high penetration value such as *Petrowax* was particularly advantageous as a means of preventing the cracking of positives.

Casts are usually strengthened by the use of cotton, wood, jute, hemp, cheesecloth, or burlap, to give bulk. These materials are dipped in the positive composition and applied back of the cast after it has reached about ⅛ in thickness.

Clarke[24] gives the following resin-wax formula: *Parawax* (m. 56°) 5, colophony 10, *carnauba wax* 1, talc 4, and zinc oxide ¼ parts. A harder wax-resin formula for pouring into the mold, but not for brushing it, is as follows: *Parawax* 8, *carnauba wax (pale)* 2, *beeswax (yellow)* 1, rosin WWW 2, and turpentine ⅕ parts.

Use of Wax Matrix in Printing

Printed pictures, etc., are treated so as to resemble oil paintings by the Thompson process.[122] The printed pictures are embossed by means of an electrotype surface obtained from a wax matrix prepared in the following manner. A copy of the picture is made transparent (by an oily liquid) and is fixed downwards in front of glass or any other transparent sheet. The back of the print is then covered with wax, and by means of a wire, or bristle brush, marks are made on the wax by following the lines of the reverse picture seen through the wax. It is necessary to transmit strong light from a source of illumination back of the glass.

An electrotype is made from the wax matrix. This electrotype is used to emboss the prints from the back. A reverse electrotype must be made from the positive if it is desired to emboss the prints from the front. Alternatively such a reverse electrotype can be made from a negative matrix by fastening the print face downwards on glass and coating the glass (instead of the print) on the other side with wax, or by securing the print face upwards and coating the face of the print. Where the canvas on the original picture is shown, an imprint on the wax may be obtained by pressing canvas upon it.

Wax in Precision Casting

An important art has developed in precision casting of small mechanical parts of metals and alloys, particularly of ferrous metals. This art in principle is similar to that used in making certain non-ferrous metal or alloy castings by dental laboratory technicians, jewelers, and manufacturers of intricate surgical instruments. A wax model is made of the small part, making due allowance for shrinkages in casting, etc. Then a ceramic mold is formed around the wax model. After the ceramic mold is formed around the wax model, the wax is melted out to get the exact contour, and the molten metal poured in the ceramic mold.

In the mass production of mechanical parts a *master pattern* or die is required to make repetitions of the wax model. This metal die is machined or cast to match the pattern with precision. Hundreds of wax forms are cast in the die, and these may be assembled in suitable arrangements so that they are interconnected by sprues. A larger sprue is formed to connect the system to the outside. The assembly of inter connected wax forms is coated over or *invested* with plaster of Paris or a sand-magnesia mixture. After the *investment* is set it is heated to melt out the wax, and then baked. The wax is reusable. The metal parts can then be cast in the finished mold, the mold centrifuged to eliminate gas pockets and to secure uniformity. After cooling, the complex form is broken up and the sprues are cut off.

Precision casting is of considerable value where the metals have too high a melting point for die casting, or where the shape is too intricate to produce it in a steel mold with the aid of hydraulic compression followed by subsequent sintering as in powder metallurgy technique. It has an advantage over the ordinary casting method in producing a cast part which has an exceptionally good surface, sharp outline, and dimensional accuracy.

The type of wax used is one which has a low coefficient of expansion, is of low viscosity, and can be easily ejected from the master pattern. A high melting paraffin, melting at about 57° (132/135° F) (A.M.P.) is of that nature. A precision casting wax made of blended waxes has also been recommended for the same purpose. A typical composition comprises equal parts of petroleum ceresin 180/190° F, and paraffin wax 132/135° F (A.M.P.), with about twenty per cent of a vegetable wax.

Dental Waxes

Manufacturers of dental supplies furnish dentists and dental laboratories with many kinds of wax compositions, such as *base-plate wax, inlay-casting wax, sticky wax, carding wax, bite wax, carving wax.* The waxes used for compounding by the manufacturer comprise paraffin of both the lower and higher melting points, carnauba, candelilla, shellac, ozocerite, petroleum ceresin, beeswax, and synthetic waxes such as "Acra Wax C," "Aerosol OT," and "Opalwax." Stearic acid is also used. Damar resin is used in the formulation of base-plate wax; and those synthetic resins which will combine with waxes are used in some dental compositions.

Base-plate Wax. Base-plate wax is a composition used in taking impressions of the mouth-gums preparatory to making the dental investment of plaster of Paris which precedes the making of the denture with artificial teeth. For base-plate wax the resin and beeswax must not only be light but standardized in color. In the compounding, the resin is preferably melted in a stainless steel kettle, and the waxes added and carefully blended by stirring. The molten mixture is filtered through several layers of cheese-cloth, or a fine mesh metal screen, and then the rhodamine or other suitable color, previously dissolved in part of the paraffin, added to obtain the desired flesh gum shade. The mixture is again filtered and poured into flat tin pans where the wax composition is congealed and remains until ready for use. The cakes are removed from the pans and heated in warm slightly acidified water, and milled on a two-roll mill, with rolls operating at the same speed to produce a perfectly smooth polished sheet of wax composition. The best rolls appear to be those made of highly polished granite, which are capable of rolling the wax in a continuous flat strip of 0.070 inch thickness or less, as required. The strips are customarily stamped before packaging.

Inlay Casting Wax. The first step in the actual construction of a cast restoration is the preparation of a pattern, usually constructed of wax. In practice, the wax is softened by heat and then forced into the cavity preparation under pressure where it is held rigid. It is then burnished and carved to the anatomy of the tooth, obtaining as near as possible an exact reproduction of the finished restoration. It is obvious that an *inlay-casting wax* must be one which has been compounded with considerable care to conform to the rigid requirements. Inlay-casting wax is prepared from paraffin or petroleum ceresin wax and a large proportion of high melting hard waxes, such as carnauba, carnauba replacement, together with a synthetic resin. Secrecy surrounds the exact composition of such waxes sold to the dental profession. However, the principle of their compounding is given in Coleman's inlay wax: carnauba 25, paraffin 60, ceresin 10, refined beeswax 5 parts, to which a suitable coloring matter is added. This wax becomes soft at 45–50° (113–122° F), and is completely eliminated from a casting mold at 250° (480° F). Most commercial inlay waxes, according to Skinner[114] start to smoke at 115–143°, and flash at 83 degrees higher.

Skinner[114] has added certain requirements to the specifications of the American Dental Association Research Associates at the National Bureau of Standards, which are given in specification Nos. 7 and 8, in the abridged standard as set forth below:

(1) The waxes should soften without becoming flaky, or laminated.
(2) They should be sufficiently plastic at a temperature slightly above mouth temperature to permit forcing them into all the details of the cavity walls.
(3) They should harden sufficiently at mouth temperature to permit withdrawal of the casting.
(4) They should curve without flaking.
(5) The color should be in contrast to that of the mouth tissues.
(6) The thermal expansion characteristics should be known.
(7) The waxes should be cohesive, but not adhesive.
(8) They should vaporize at a temperature compatible with normal casting practice without leaving residue other than carbon.

Sticky Wax and Other Waxes. *Sticky wax* is sticky as the name implies and is used in dental laboratories for the preparations on investments, such as making ridges, and for general laboratory technique. Sticky wax is prepared from beeswax, ceresin, or a microcrystalline petroleum wax, "Aerosol," and Venice turpentine, and cast into sticks. *Carving wax* is a wax that is prepared hard so that it may be carved in the mouth in making gold inlays. It is harder than the regular inlay-casting wax and is used particularly in making gold inlays, and as a means of taking well defined impressions in dental laboratory technique. Carving wax must be non-crystalline, of high fusion point, cohesive, and hard, though free from brittleness. It is made from a mixture of high melting waxes including carnauba. *Carding wax* consists mainly of a high penetration petroleum wax, and is extruded in suitable ribbon shape for mounting artificial teeth. *Bite wax* is a wax that must have a high plasticity at normal temperature, and yet have cohesive instead of adhesive properties. Beeswax is used for the purpose, also beeswax and petroleum ceresin 170/180° F (A.M.P.). *Temporary filling compounds* are made of gutta percha with less than 1 per cent of wax.

Wax Portraits

The ease with which wax can be worked has insured its use throughout the ages in modelling. Modelling in wax, says Bolton,[12] has always been done for one of two reasons: either as a means to an end or as an end in itself. During the Renaissance, doubtless, wax was used for both reasons, but more often as a means to the end. The bronze medals of Pisano owe their delicacy to the fact that they were first modelled in wax. Wax objects of art may be grouped into three classes: statuettes, allegorical subjects, and portraits in relief. The first class appears to have no examples in America, and but few in Europe. The second class, allegorical figures in relief, has had many examples in England. According to Bolton,[12] the greatest artist in this work was Flaxman, many of whose subjects were afterwards translated into pottery by Wedgwood for his jasper ware. Flaxman also made many portraits which were put to the same use.

In the third class, portraits, the earliest English portrait known is a beautiful one of King James I, which was done by Abdonio Allesandro, the younger, an Italian who lived between 1550 and 1650. Another sixteenth century wax portrait modeller was Leone Leoni, who left us a portrait bust of his friend, Michael Angelo. In France there are a number of wax portraits (by the artists Clouet, Dupre, and Benoits) preserved in the Cluny Museum. Patience Wright was the first American to model portrait heads in wax. She started on this type of artistic work at Bordentown, New Jersey, in 1769, but moved to London in 1772, where she was acclaimed as the most skilled in the art by Horace Walpole. She made many models in life size of English notables; her full length portrait of Lord Chatam found a place in Westminster Abbey after his death. Her models were also made in the round. Her relief of George Washington in white wax is the best example of her work in America. Her son, Joseph Wright, returned to America and modelled in wax the designs for the first coins minted in the United States.

Waxes are so frail, are so subject to the action of heat and cold that not many of the earlier objects of art have come down to us intact. The artists always worked with their secret formulas, which were not only in white but in all sorts of colors. Vasari, the chronicler of Italian painters, writes of the mediæval method of preparing wax for use: "To render softer, a little animal fat and turpentine and black pitch are put into the wax, and of these ingredients it is the fat that makes it more supple, the turpentine adds tenacity, and the pitch gives it a black color and consistency, so that after it has been worked and left to stand it will become hard." Many portraits were done, as Flaxman's allegorical figures were, in white wax. In the Lewis Harcout collection in England there is a beautifully modeled portrait of William Pitt in pink, done by Peter Rouw, the best of the English artists. Wax portrait modelling also flourished in the Victorian era. The Essex Institute at Salem, Massachusetts, has examples of early wax portraits. One of these done by Rauschner, a Dane, is of a family group, mounted as usual on glass painted a slight seal brown on the outer surface. The wax of his portraits is colored all the way through, according to mediæval recipe, and only the small parts, like the eyes, eyebrows, and slight shadows, are painted in. Some sculptors modelled their portraits on velvet, either in color or in white wax. Fine qualities of white lead were mixed with wax to produce opaque whiteness, but the compositions turned yellow in the course of time from sulfur gases. Hughes, an English sculptor, came to America and modelled reliefs in wax that would remain white, but never revealed his formula. With the death of Hughes the art languished in America, although there have been many attempts made to revive it.

Modeling Flowers in Wax

"The art of imitating flowers in wax is perhaps the most beautiful method known of preserving a life-like representation of garden-gems, as the form, color, and texture can be imitated to perfection" wrote Worgan[132] in 1867. He records that the wax supplied for such purposes is prepared in sheets, and directs how it should be used. "Should you wish to imitate a thin petal, take the *thin wax;* for a thick one take the *thick wax;* and should you require a still thicker petal, double the wax together."

The wax used in modeling flowers was white beeswax, and the sheets were not only available in natural white color, but also in tints of green, and a shade of light yellow. The colors as a whole were applied from powders of white, chrome yellow, carmine, ultramarine blue, prussian blue, vermilion, and magenta or solferino pigments, and numerous tints of such colors. The dry color was always rubbed on the modeled wax with the fingers.

Worgan[132] gave directions for fashioning imitation roses: "Cut the larger-sized petals out of *thick* white wax or thin wax doubled—the two smaller sizes from *thin* wax; rub them with the sofrano rose bloom, tint some of the petals with light pink powder, also rubbed on, taking care to leave a portion of the petal uncolored at the base, as this is the part you require to join to the foundation." The color referred to was one of a great many supplied by the H. H. Dickinson Pharmacy, of Brooklyn, N.Y., to artisans of that time.

The industry of modeling flowers in wax is now a highly specialized one and comprises a large number of operations performed by separate hands. The processes consist of cutting up the various fabrics and materials into shapes suitable for forming the leaves, petals, etc. This is done by scissors, or by mechanically operating stamping presses. The veins of the leaves are impressed by means of a die, and the petals are given their natural rounded forms by buffering irons of various shapes. The next step is to assemble the petals and other parts of the flower, which is built up from the center outwards and then the flower is mounted on a stalk formed of brass or iron wire wrapped with suitably colored material, and leaves are fastened on to complete the spray. In artificial wax flowers the fabric materials are coated with wax. A composition suitable for producing such flowers, according to Fuchs,[38] consists of the following: balata 38, gutta percha 3, wood tar or rosin oil 4, carnauba wax 12, beeswax 42, copal resin 3, organic coloring matter 3, and aluminum palmitate 1, parts. It is also possible to modify the composition by leaving out the gutta percha and copal resin. The ingredients are melted together at a temperature of about 150°.

The modeling of plants of wax, as conducted by museums, involves squeeze mold casting, since this gives the exact reproduction of the sprays of leaves and flowers. A full description of the art of making a squeeze mold for museum work is given by Coleman,[28] to which the reader is referred. The description of squeeze mold casting given below refers to the art in a more general manner.

Squeeze Mold Casting. In order to reproduce objects one may employ what is known as squeeze molds made of metal, plaster or thermoplastic, and waxed cloth as a positive to receive the impression. For example, in reproducing sprays of leaves and flowers, the leaf may be placed in a clay bed and the first half of the mold made by means of liquid plaster being poured upon the leaf. It may be necessary to reinforce the mid rib of the leaf by means of a fine wire, so that a similar impression can be made from the reverse side for the second half of the mold. These molds are known as squeeze molds. The mold and counter-mold of plaster may have suitable grooves so as to facilitate matching them up, and be provided with a strap hinge and handles.

In using a squeeze mold it sometimes becomes necessary to soak it in hot water so as to prevent the positive from chilling. The waxes used for the positive are beeswax and fully refined paraffin; *e.g.*, a blend of *paraffin wax* (m. 62°) 1, and *yellow beeswax* 7 parts. The positive material, in this instance waxed cloth, is placed between the faces of the leaves, and the wire reinforcement described above is made long enough to form the stem.

Casting a Wax Leaf. The following method is one that has been described by Coleman[28] as used in the production of plants of wax at the American Museum of Natural History. When leaves are to be cast from a squeeze mold, the mold must be soaked in hot water and used while warm and moist. Heat keeps the wax from chilling until it fills the mold and moisture prevents it from adhering to the plaster. A film of cotton is laid upon one side of the mold—better the concave side if either one is so. A piece of cotton-covered hard iron wire is laid along the line of the midrib, with its end projecting from the stem. Melted wax, tinted green with oil color, is then poured upon the upper part of the mold, and squeezed down upon it. The whole is plunged into cold water, opened and the cast removed.

The wax should be, according to Coleman, bleached beeswax to which is added about a tablespoonful of Canada balsam to each quart of melted wax, the object of the balsam being to toughen the wax. Wax should be melted in a double boiler. The oil color is thinned with a very little turpentine, and thoroughly stirred into the melted wax; this gives the body color of the leaf to be imitated. Foliage for imitation may be preserved by the following composition: formalin 15, water 35, and glycerin 50 parts.

After removing a cast from a mold, the mold is set aside to dry and before it is used for another casting it should be hardened by boiling in a strong solution of borax for about twenty minutes or soaking in melted paraffin for about the same time.

Waxes as Embedding Media for Micro Technique

Paraffin alone does not make a satisfactory embedding medium for animal or vegetable tissues, since the ribbon which is cut with a microtome from the block which holds the tissue, will curl or roll in the cutting, making it impossible to handle the specimen properly for microscopic examination. It is for this reason that a paraffin-bayberry wax-rubber mixture has been used for both infiltration and embedding of tissues. Recently Groat[55] found that a more satisfactory medium can be prepared by blending a synthetic resin of low viscosity with the *paraffin* or *ceresin* used. For example he cites a particular blend of paraffin, m. 56 to 58°, with a water-white hydrocarbon resin (LX–291) produced by the Neville Co., Pittsburgh, Pa., as very satisfactory for the purpose. Excellent sections, which ribbon well, of any desired thickness below about 20μ can be cut at room temperature.

The compositions of the paraffin-resin media are indicated here by the percentage by weight of resin in the mixtures. Hardness of the media increases as the content of the resin increases. The mixtures are most readily prepared by blending the weighed portions of paraffin and resin at a temperature of about 170°, and filtering. A paraffin oven set at 59° is satisfactory for holding any of the melts.

Best results are obtained by infiltrating tissues in pure paraffin, in a 5 per cent mixture or in a 10 per cent mixture, and embedding in a harder medium. With a 50 per cent solution as the embedding medium, sections of 1 were the only ones that would ribbon. Invariably, as the medium becomes harder the range of thickness of sections which can be cut well becomes narrower and shifts downwards.

It is desirable to use a wetting agent in the fluid used to float the sections on the slide, especially for the thinner ones where incorrect infiltrating and imbedding media may result in production of fine creases in the tissue of the section.

WAX APPLICATIONS TO PAPER PRODUCTS AND FOILS

The largest use of wax, particularly petroleum waxes, is in impregnating and/or coating cellulosic materials. The consumption of only the vegetable waxes is exceeded by the polish industry. The greater part of the wax consumption by the "paper converters" is for the purpose of paper packaging. There are many ways in which wax is applied to paper material, and these methods will be referred to later. Wax is used for waterproofing cardboard as well as sheet paper. The paper converters use continuous machines which wax and slit the paper to the required widths. Squaring sheets to specified size is an operation in addition to slitting. A wrapping material is printed from a roll of paper slit to the required width, by means of a rotary electrotype which is inked, and then the printed paper is paraffined or otherwise coated with wax. Waxed bread wrappers are made in this manner, the paper being slit transversely to the required length for wrapping the bread loaves. The whole process of printing, waxing, and wrapping is automatic.

Drinking cups made of paper are waxed, as are paper milk bottles. Paper mills use wax emulsions for sizing special kinds of paper. The lithographed pages of the leading magazine publications are usually sprayed with an infinitesimal amount of wax to prevent them from sticking to each other. Wax is extensively used in the manufacture of paper liners for glass jar closures. Army ration boxes are waxed. Wax is used as the principal constituent of some of the heat-sealing foils. Carbon papers which are used in copying from pencil, pen, and typewriter are manufactured with a colored wax foundation. Many of the waxes used in the arts described above are blends of petroleum wax with vegetable wax, and occasionally with resin, or rubber. A modern use for wax is as an adhesive in laminating paper materials.

Protective Paper Packaging

There is a constantly growing demand for paper material which is water-repellent and moisture-proof, particularly by those who are engaged in paper packaging commodities. Paper may be made water tight by filling up the minute spacings between the fibers with wax. This may be done in the industry by what is known as "dry-waxing," but to make the paper substantially moisture-proof it is necessary to resort to "wet-waxing," in which case the application of the wax is in a continuous film, with only enough wax impregnated in the paper to provide a bond for the coating. A third method of imparting both waterproofness and resistance to water vapor penetration is to use two sheets of paper with a layer of wax in between. Wrappers for cigarettes employ a laminated paper of this description, in which two sheets of soft paper have a black microcrystalline petroleum wax between them in a continuous film; the resultant wrapping material has a water-vapor transmission rate which compares very favorably with the metal foils for the purpose. This same principle of lamination has been applied to other types of wrapping materials, where exterior water tightness is not required.

Exterior coatings of wax are used on paper for bread wraps, cake wraps, candy wraps, butter cartons, cottage cheese cartons, etc. Wax is applied to containers already fabricated, such as individual drinking cups, paper milk bottles, and food ration boxes. Large quantities of petrolatum and of slack wax are used by the makers of paper-board containers. Eighty per cent of the petroleum waxes consumed are used for packaging purposes.

Fruits are often wrapped with waxed crystalline papers, which reduce loss of weight and pitting, although they do not prevent the fruit from molding. The same is true of the crystalline paper wrappings used with grapes.

Packaging of Frozen Foods. Waxed parchment and waxed cartons are widely used in the packaging of frozen foods, as the frozen food processors have been quick to see the advantage of a wax coating. Waxed parchment is used for wrapping fruits and vegetables, and the wraps are heat sealed and placed in waxed paper cartons. Berries and sliced fruits for freezing are usually packed with sugar or heavy syrup and hence require liquid-tight containers. Heavily waxed cylindrical or cup-shaped cartons are used for the purpose, as they are easily filled and leak-proof. Empty cup-shaped cartons meet with favor with the processor since they nest well, although neither the cup-shape nor cylindrical cartons are as economical of freezer space as cubical cartons. The latter, heavily waxed and heat-sealing, are easily filled and may be compactly packed in the freezer.

A popular type of package for fruits and vegetables is the folding rectangular carton, heavily waxed. A shallow form of this carton, lined on the inside with a sheet of moisture-proof cellophane, or specially coated vegetable parchment, is used for packaging all kinds of vegetables, including corn-on-the-cob and asparagus tips. Tressler[123] states that when such cartons are filled, they should be overwrapped and heat-sealed in either moisture-proof cellophane or specially coated vegetable parchment. Ground meats may be packed in heavily waxed paper-board cartons, or waxed folding cartons, adequately moisture-vapor-proof lined on the inside. Meats are suitably wrapped and packaged in waxed rectangular folding cartons lined with moisture-proof cellophane or parchment.

Production of frozen foods in 1944 approximated 600,000,000 pounds, compared with 450,000,000 pounds in 1943.

Methods of Application of Wax to Paper. Wax may be applied to paper in various ways, the method chosen in accordance with the specific needs. Various methods are here mentioned.

(1) As an emulsion in the beaters at the paper mill. This method has definite limitations.

(2) As a spray on paper material, in which the wax snow spreads well if the paper is warmed. The spraying is usually done by a Grammer spray machine.

(3) As a coating to paper or paper board, applied on one or both sides by a roller. The roller may be smooth, grooved, or wire wound.

(4) A cardboard material is impregnated in a paraffin bath, and then directly dipped in a finishing-coat bath of a special wax held at a lower temperature.

(5) The article of paper material may be flushed with molten wax by a flushing-type machine.

(6) Immersion of the entire paper sheet, or board, in a wax bath. This is common practice. A sealed, filled carton is given a single dip in a wax bath.

(7) Cartons sealed at one end may be dipped in wax, oven dried to spread the wax and finally heat-sealed. This is known as the Dacca method.

(8) Lamination of paper material to similar paper stock or to cellulosic or non-cellulosic films by using a microcrystalline petroleum wax of a selected sticky grade.

A type of laminated paper that has come into extensive use for refrigerater locker packages is known as "locker paper" and consists of a sandwich of two sheets of glassine with a *petrolatum wax* in between. The glassine sheet usually is either 45 or 55 pounds to the ream. Locker paper has a very low moisture-vapor penetration value, which does not change when the paper is creased in the wrapping of foods for the freezer lockers.

Wax in Paper Sizings

Material commonly used by the paper manufacturers in sizing papers are colophony, paraffins, montan wax, alum, sodium aluminate, and soda ash. *Paraffin* is the wax most commonly used in waxed sizes. It is not saponifiable and must be prepared for use by emulsifying it in water, thus obtaining a water dispersion of wax particles surrounded by a protective film which keeps them from agglomerating into a solid mass. There are numerous emulsifying or assisting agents. *Montan wax* acts as a stabilizer of emulsions when added to paraffin. Where paraffin wax is used as a "size" the paper necessarily contains very little of it, since after all most of the sizing materials that go into the beater are run to the sewer; only those adhering to the fibers find their way into the formed sheet. Hence, paper sized with paraffin has little of the feel of either a wax impregnated or wax coated paper.

Sizing with rosin has varied from completely saponified rosin to a mixture of about ½ rosin soap and ½ free rosin carried thereby as an emulsion. So-called rosin emulsions are really suspensions of finely divided rosin. Mixing *paraffin* or *ceresin* with a rosin emulsion, and later using alum and a pH of 4.9 gives a 50 per cent saving in rosin.

Bennett[11] gives a recipe of a paper sizing which is as follows: rosin 70, soda ash 7, *beeswax* 2, and water 21 parts. The ingredients are boiled together until a sample solidifies on cooling. This may be shipped solid, to be dispersed in hot water when needed.

The amount of sizing is dependent upon the kind of furnish used in the paper making. Book paper has 0–2 per cent, writing paper 2–3 per cent, kraft 1½–2½ per cent, wrapping 2½–3½ per cent, wall board 2–5 per cent, and container board 3–5 per cent size. The ratio of wax to rosin in sizing is commonly about 1½ rosin to ½ wax.

Wax in Greaseproof Paper. Paper is greaseproofed by (1) treating at least one surface with a material which contains no wax, (2) sizing the surface with a non-wax material and then waxing the sized paper, or (3) treating the paper directly with a wax composition. An example of (1) would be the treatment of paper with a solution of rubber hydrochloride; of (2) the priming of a paper sheet with bentonite and cooked starch, the filming of the treated surface with zein, and finishing with about 2 to 4 pounds of wax to 2880 square feet, as in the process of Schur[109]; of (3) the dipping of the sheet in a wax mixture, passing it over a heated roll and then a chill roll.

The number of formulations published for greaseproofing is tremendous. A typical one is that of Cable[19] who states that a paper can be made greaseproof by dipping it in a wax mixture heated to over 56° and passing it over rolls heated to the same temperature followed by chilling with rolls kept at a temperature of 4°. The wax mixture comprises anhydrous lanolin 6, paraffin wax 2, white petroleum jelly 2, and white spirits 4 (or less) parts by weight. To mask the odor 1/16 part of eucalpytus oil is used.

Waxed Paper Wraps. A waxed paper, translucent and pliable, is made for automatic wrapping and sealing machines, by super-calendering a non-greaseproof paper sheet with molten *petrolatum* of high melting point, prior to the final waxing operation. The automatic wrapping machines usually fold portions of the waxed paper on itself and seal the fold around the wrapped article by melting the wax on the sheet.

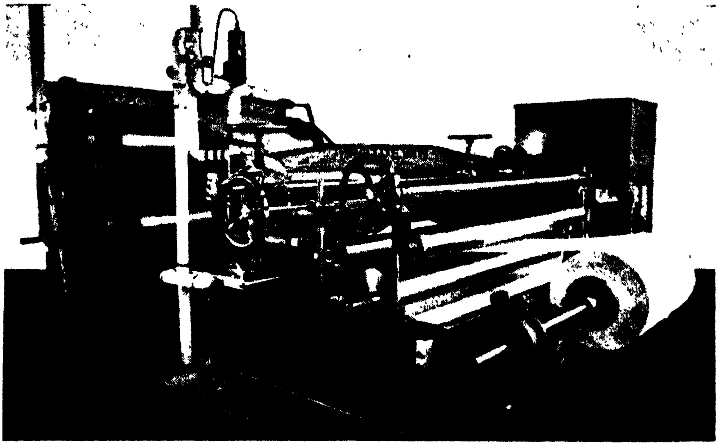
Briefly the process of waxing, according to Dodge,[37] is as follows: The paper to be treated is in the form of a mill roll, and is guided by means of two rollers into contact with the surface of a fountain roll, the lower portion of which is immersed in a bath of melted petrolatum. The petrolatum is contained within a tank provided with heating elements, such as steam pipes, for maintaining the petrolatum at 150–175° F. As the fountain roll revolves, it picks up a film of molten petrolatum, the excess of which is doctored off by means of a roll or rod doctor. The film of petrolatum remaining on the fountain roll is transferred to the underside of the paper. The paper sheet will thus be impregnated with petrolatum, preferably to the extent of $1\frac{1}{2}$–$2\frac{1}{2}$ per cent by weight. After leaving the fountain roll the web passes around a steam-heated roll and thence is led by two guide rolls to a rewinder, where it is rewound at the rate of 500 ft per minute. The petrolatum-impregnated paper is then subjected to a waxing operation by passing it through a molten bath of wax in accordance with known practices (see p. 439).

For high quality waxed paper wrap material used in packaging fine cakes, etc., it is advantageous to use a petroleum wax with a substantial, if not predominant, amount of microcrystalline wax so that the creased or crumbled sheet of waxed paper will not show a rupture of the wax coating. It is possible to prepare commercial waxed papers with a water-vapor transmission rate value as low as 0.2 gram per 100 sq in per 24 hours at a temperature of 100° F, and a relative humidity of 95 per cent on the wet side.

Waxes Used in Waxed Paper Art. The wax most commonly used in waxed paper art is *fully refined paraffin.* The range in melting point is from 127° to 140° F by the English method of determining melting points. In making a waxed paper for bread wrapping it is customary to use a sulfite sheet of 20 to 25 pounds weight to the ream, and wax this up to 33 to 37 pounds to the ream. According to Padgett[96] the addition of a small amount of montanic acid ester (*I.G. Wax*), Vistanex, *Opalwax,* or other very high melting wax to the paraffin will improve the tensile strength of the wax and increase the strength of the seal to the package.

Waxed wrappers for packaging potato chips and other dry food materials that require hermetic sealing may be prepared by treating glassine paper with a hot melt of ethyl cellulose, resin, and wax. The coating material must be of such a nature that the treated paper material will have a very low coefficient of water-vapor penetration, will flex under a wide range of temperature, and produce a tight strong seal under application of heat. Rubber-wax blends are also waterproof and produce a lustrous finish to the wax coating.

The value of a blend of paraffin wax and microcrystalline petroleum wax in preparing coated paper for wrapping foods is set forth in a letters patent of Adams and MacLaren.[4] The mixture is prepared with not more than 10 per cent of microcrystalline wax having a melting point above 63° (145° F); the latter not having more than 10 per cent of oil, in order that the mixture contain no more than 2 per cent of occluded oil. In the prior art—*beeswax, japan wax, ozocerite,* resin, etc., were added to *paraffin wax* to act as inhibitors to coarse crystals of paraffin forming when the wax was chilled. A thin film of paraffin, even if continuous, is never more than 50 per cent impermeable because of the interlacing fine needles. The inhibitor greatly increases the impermeability.



Courtesy Potdevin Machine Co.

FIGURE 30. Typical waxing plant installation. The machine has steam and water connections, various helpful accessories of operating instruments, and electrical controls.

Waxing Paper and Pasteboard. The terms "dry waxing" and "wet waxing" are frequently used in the paper and pasteboard industries to denote not simply the method of application of the wax to the paper material, but to denote the character of the waxed surface. For many purposes it is desirable to apply an exceedingly thin film on the surface of the paper material and hence dry waxing is resorted to. Examples are builder's papers, chewing gum wrappers, fish paper, florist's paper, fruit wrappers, labels, etc. The addition of a very small amount of a high melting microcrystalline wax of the harder kind will prevent waxed tissues from blocking.

In the waterproofing of pasteboard material the pasteboard is passed through a bath of *paraffin.* The addition of a little *aluminum palmitate* to the paraffin will keep the pasteboard from darkening.

The waxing of paper may be carried out on a rather simple machine, as shown in Figure 30. The roll of base paper is supported on a roller at one end of the machine. From this roller it is lead through a trough containing the wax that is kept molten by a suitable heating device. As it leaves the trough, scraping devices remove the excess wax and control the film thickness. The sheet then passes over chill-rolls, which set the wax, and on to the rewinder. Depending upon the requirements, the rewound coil is either sheeted or cut into specified widths on a slitting machine. (Figure 31.)

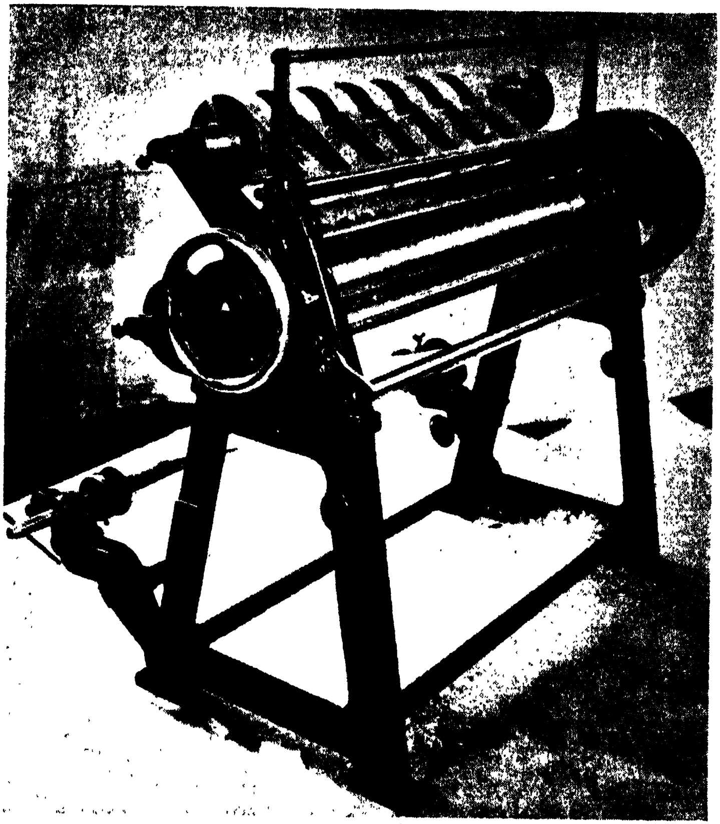

Courtesy Charles Beck Machine Co.

FIGURE 31. Razor blade slitter and rewinder.

In the printing of colored illustrations for magazines there is apt to be an offsetting of the colored inks to the white sides of the sheets as they are piled freshly from the press. By mechanically spraying the sheet with a fine cloud of wax by a Grammer spray machine this offsetting is avoided. The type of wax required is one that is hard so that the droplets are not flattened and smudging is avoided. It may be brittle; that is, hard, but of low tensile strength.

Moisture Proofing Non-fibrous Wrapping Material. Various methods have been proposed for the moisture proofing of regenerated cellulose film, exemplified by cellophane, for the purpose of using the "finish sheet" for wrapping foodstuffs, drugs, tobacco products, and other items. Cornwell[30] proposed a transparent coating with a cellulose resin base, one which will firmly adhere to the base sheet so that the coating and the sheet remain inseparable. Cornwell's coating is prepared from a cellulosic lacquer base, plasticizing resin, plasticizer, and wax, together with a solvent. Very little wax is used in the coating composition. Charch and Hershberger[22] accomplish a similar result with a composition comprising a cellulosic lacquer base, pale crepe rubber, and paraffin wax; the latter is the chief constituent.

The lacquer base of Cornwell is nitrocellulose, cellulose acetate, benzylcellulose or a film-forming synthetic resin. The plasticizer is dibutyl phthalate or its equivalent. The wax may be any of a number of waxes including *paraffin* of a high melting point. The non-volatile wax blending agent may be a blown oil, like blown rapeseed, or a resin such as dammar or ester gum. With the cellophane so coated, the contiguous surfaces may be effectively sealed together by the application of methyl Cellosolve, methyl acetate, acetone, etc. A mixed solvent is used in the cellophane coating composition, which contains ethyl acetate, butyl acetate, and toluene.

A claim in the letters patent of Charch and Hershberger[22] for their coating gives the formula of the composition as pale crepe rubber 7, pyroxylin (51 sec) 10, and *paraffin* (m. 60–62°) 83 parts. The coating fluid contains 90 per cent of a solvent mixture of 60 per cent toluene and 40 per cent amyl acetate. They specify a coating on both sides of 0.00001- to 0.00015-inch total thickness in the dried state. The cellophane so coated may be heat-sealed by means of a hot iron in two or three seconds; making the wrapping tissue easily amenable to many types of packaging.

The wrapping of ordnance has provided the largest use for microcrystalline waxes. For example, the wax coating of cellulose acetate on scrim, for Type I demanding a high bursting and tearing strength to the wrapping of metal parts, etc., as outlined in "Wrapping, Greaseproof U.S. Army Spec. No. 100–15, issued 10 Feb. 1944." Type II calls for a medium bursting and tearing strength which is met by waxed acetate on kraft. Type III calls for a low strength, which is met by waxed cellophane and scrim. Microcrystalline waxes are also used for "AXS–1015 Wax Dip Coating" of same specification.

Metal foil suited to wrapping foods and other commodities may be coated with a thermoplastic, which has petroleum ceresin wax in its composition, at a temperature above that of the melted mixture and according to Laufer[77] then lacquered to prevent offsetting, and without destroying its heat-pressure sealing efficiency.

Waxed Drinking Cups. Paper cups for drinking are made with plain or pleated walls, and are then coated by dipping them in molten wax. However, if a warm drink is placed in a paraffined cup, the wax soon softens and the cup is apt to collapse. Therefore it is desirable to use a wax of high melting point. Reifsnyder,[103] in a patent assigned to the Tulip Cup Company, suggests that paper receptacles be impregnated with a compounded wax comprising *carnauba* and *paraffin waxes; e.g.*, carnauba 20, and paraffin (m. about 140° F) 80 parts. Since the melting point of carnauba is about 180°, the compounded wax would melt at 160–170° F. Smaller amounts of *I.G. Wax Z* are more effective than carnauba, and the paraffin wax can be effectively replaced by a mixture of lower melting paraffin with high melting *microcrystalline petroleum wax*, to produce a superior high melting coating wax for coffee cups and the like.

The customary coating procedure for paraffined cups is as follows: the mixture of waxes is heated to about 250° F, then applied in liquid form to the cup, preferably only to a portion of the cup, and while the coated portion is still hot, the cup is subjected to heat so as to spread the wax over the whole surface. Enough melted wax is poured into the cup to fill it about one-eighth or one-fourth full, then by immediately emptying the liquid from the cup and giving the cup a twist of one-half to a full revolution, a coating from bottom to rim results. By putting the cup into an oven heated at 180–200° F for about three-fourths to a full minute, a good penetrating coat results that waterproofs the cup so that it may withstand hot liquids to a temperature of about 170° F. The most modern method involves a continuous instead of batch process.

Waxing Paper Containers. Paper, strawboard, and like containers are impregnated with wax by dipping them in a bath of melted wax kept at 190–210° F temperature. Usually the containers are maintained in the bath for about 30 seconds, and then are suspended about 10 seconds to drain. In their manufacturing production line the containers are placed in cages pivotally suspended between endless chains, and are moved horizontally through a bath of melted wax, and through an inclined path to permit draining before discharge. The cages consist of U-shaped supports carrying a base of netting or like material, and a hinged lid or cover resting on adjustable nuts on the supports. The lid is raised to allow containers to be fed to the cage by engagement of projecting arms on the lid with brackets fixed to the front of the machine. The cage is tilted to discharge the containers by arms engaging a bar at the rear. The bath is adjustable vertically and is heated by burners or by a steam coil.[69]

In Reed's process[102] a paper container, fabricated from a white bleached sulfate or other suitable taste-free paper base, is subjected to a moisture-proofing material at a temperature at least as high as 212° F, so that the paper is impregnated, and the container is then subjected to a bath of paraffin wax at a temperature below 212° F, when it is later chilled and made ready for use. Paper milk bottles are treated in this manner. This method has come to be known as a "double wax dip," and is being extensively employed in the waterproofing of cartons used for rations, ammunition, and dehydrated foods shipped overseas from the United States.

Containers for cheese, butter, and ice cream must be liquid tight. The liquid-tight container is made up of a fine grade of bleached sulfite of sanitary quality, and usually coated with wax after it has been colorfully decorated.

Bottle Cap Liners. Paper material for lining bottle caps is waxed in order to facilitate easy removal of the caps from the glass containers. Generally speaking these liners consist of a kind of protective facing material mounted on a cushion liner of gray pulp, white pulp, or composition cork. The protective facing material can be an oil paper, varnish coated paper, vinylite coated paper, pliofilm, glassine, or just plain wax. The cheapest oil paper liners are simply coated with *paraffin*; varnished paper liners are usually coated with an artificial *ceresin*; and composition cork with either *paraffin* or *beeswax*; the latter if resistance to oil is needed. Non-slip waxes are used for liners in lug caps and the like. Various waxes are used in bottle cap liners depending specifically on the type of product for which the cap is provided. The waxes include *paraffin* (128–130° F), and (138–140° F), *yellow beeswax, white beeswax, petroleum ceresin wax, petrowax, carnauba wax, candelilla wax, Opalwax, I.G. wax Z*, etc. In general it is desirable to use waxes of high melting point, as the containers are often filled with a warm product, or the jars after filling are washed with warm water, and it is necessary to avoid having the wax stuck to the lip of the glass.

A waxed paper liner for sealing mineral water may be made by coating a sulfite paper with *paraffin* 17, and *ozocerite* 13 parts. Either refined paraffin melting at 123 to 125° F or 128 to 130° F may be used.

Waxing Ration Boxes. The Quartermaster Corps. of the U.S. Army specify the use of a blend of paraffin-type and microcrystalline type waxes for wax dipping the K-ration or other ration boxes. The packages after dipping are drained in an angular position to eliminate accumulation of wax on edges. These are the individual ration packages which hold concentrated foods and are generally very small in size.

A double wax dip method for waterproofing cartons of rations, ammunition, and dehydrated foods is resorted to. The impregnating is often done with refined paraffin or slack wax, while the finish dip is made with the wax blend. Microcrystalline petroleum wax has proved advantageous for military packaging because of the high melting point obtainable and its greater ductility which prevents chipping at low temperatures. Petroleum waxes in themselves do not provide greaseproofness.

Butylene Polymer—Wax Blends as Coatings for Wrapping Films. *Paraffin* can be blended with polyisobutylene, and the polymer-wax blend can be applied to cellulosic, or non-cellulosic transparent film material to produce transparent, air tight wrappings for cheeses, etc.; the ends may be readily sealed by slight heat and pressure. Polyisobutylene is known as "Oppanol" when made in Germany, and as "Vistanex" when made in the United States. Butyl rubber is closely related to it. The polymerization is conducted by the refinery at a low temperature with the aid of boron trifluoride as a catalyst. The wrapping material known as *Parafilm* has an underlying cellophane sheet, or similar sheet, on which the wax compound is coated. Parafilm can be printed upon on the unwaxed side, and provides a very flexible sheet for wrapping, and one which can be heat sealed for the protection of various articles of food, such as cheese, etc.

The coating to the film material may be applied by the method of Abrams and Wagner[3] in which the transparent sheet is made to pass between a lower heated cylinder and an upper cylinder. The distance between the two corresponds to the desired thickness of the coating. The task of the upper cylinder is to spread the coating evenly on the base material. Immediately following these two cylinders is a third one, which latter is water cooled and its purpose is to solidify the applied coating, so as to permit immediate rewinding of the finished sheet material.

To increase the hardness of the wrapping film, resin can be advantageously introduced into the butylene-polymer-wax blend, thereby increasing the luster, and permitting the film material to be handled without its "blocking." Various commercial resins are usable for the purpose, *e.g.*, Nevellite, Staybelite, Aroclor, Damar, etc. An example of a Vistanex-wax-resin composition for coating film is the following: Vistanex 10, paraffin wax 35, and resin 55 parts. The preferred wax is one with 134–136° F melting point. The Vistanex, a product of the Standard Oil Development Co., can be dispersed in wax in a manner similar to wax-rubber dispersions. Buna S, which is a polymer of butadiene compounded with a lesser amount of styrene, and a little *stearic acid*, can also be blended with wax and resin, but not as readily. In the Thomas process[121] the polymer of butylene (molecular weight 50,000–100,000) to the extent of 5–15 per cent is dissolved in a hydrocarbon solvent and then homogenized with paraffin wax; the homogenizing is carried out in an attenuated stream subjected to a substantial centrifugal force, and the solvent later removed by heat and vacuum. Such a composition is applicable to cellulosic material to make it moisture-proof, gas-proof, refrigeration resistant, flexible, etc. It is also used in wrapping and packaging frozen foods.

Carbon Papers

The principle used in the manufacture of carbon papers, also called "carbons," is that of coating one side of a suitable paper sheet material with carbon-paper ink, which is a mixture of wax, color and oil. The amount of ink applied to the paper is regulated to such a proportion, that when the sheet is placed downwards over white paper and beneath the sheet upon which the writing or typing is done, the pigment may be transferred by the pressure of a pencil, pen or type to the lower sheet, and an exact copy of the writing obtained.

Theoretically speaking, the ideal carbon paper ink, according to Olsen,[95] would be one made from a wax carrying color, and containing no oil. Such a formulation would not be practicable as the finished composition would be too hard to release an impression. Therefore a precise balancing of the three ingredients, oil, wax, and color, must be brought about to yield an ink with the desired characteristics. Oils are chosen for their non-drying properties, since it is very important that the oil will be resistant to both drying and oxidation, otherwise the coated carbon sheet will harden in the course of time, and refuse to release a marking. The prime function of the oil is to produce softness and compactness of the ink, whereas that of the wax is as a vehicle to carry the color, and keep the ink from completely soaking into the paper.

Type of Paper for Carbons. For pencil carbons a white paper of rag and chemical pulp is suitable; for pen carbon papers only tinted rag paper is used; and in the case of carbons for typewriters the paper must have a texture so as to receive the blow of the type uniformly and yield clear imprints without the application of undue force. One method which has been suggested to bring about increased flexibility and longer life to the paper is to treat the paper prior to coating with the ink by immersion in a solution of gutta percha in carbon tetrachloride, and then drying it.

Pigments and Vehicles Required. Carbon black from natural gas is used as the black pigment for certain kinds of carbon paper; hence the name "carbon." The name is retained even when the paper is coated or printed with a colored pigment. Although carbon black has a good covering power it transfers as a brownish black, and hence it must be toned by a powerful jet black dyestuff, such as nigrosine. The waxy ink is referred to as the foundation, and more commonly as "dope." If lampblack is used it will comprise less than 20 per cent of the formula, whereas carbon black with oil-soluble toners might comprise 25 per cent of the dope. With a strong hue such as crystal violet the dye would amount to only 3½ per cent of the mix. The dye is first dissolved in double its weight of red oil. Equal proportions of wax and vehicle (oil) are used together comprising 75 per cent, or more, of the ink ingredients. The vehicle is a petrolatum oil, or a non-drying vegetable oil. Any of the higher fatty or wax alcohols are of particular value as vehicles, *e.g.*, ceryl alcohol, stearol, oleol, palmitol, lauryl alcohol, mysticyl alcohol, jojoba oil, and the like, when they are available. Sesame oil is well suited to use with some of the coal tar lakes. Red is usually made from lithol or geranium lakes ground in oil. A water-soluble wax such as *Carbowax* has value as an ingredient in copying inks.

The Wax Foundation. *Carnauba* and *candelilla wax* are used effectively with *crude montan wax* as foundations in recipes for "dope." *Crude montan wax* is an excellent solvent for nigrosine. *Beeswax* is also used with carnauba to give the dope certain desirable physical properties in transfers, such as sharp imprints, that are not obtainable with the harder and more resinous waxes. *Paraffin* (m. 128/130° A.M.P.) and *stearic acid* in very small amounts aid in producing smooth working inks. In these wax mixtures oil-soluble toners, carbon black, methyl violet, etc., are incorporated. The vehicle is petrolatum, sesame, or sperm oil. Red oil (oleic acid) is used in cheaper dopes.

Hattori[58] proposed a coating material for preparing carbon paper, comprising a barium soap with oil and pigment added; *e.g.*, *barium stearate* 3, castor oil 2¼, and violet lake 3¼ parts. He states that soaps of aluminum or magnesium may also be used to replace the usual wax constituent of the carbon ink. However this may be, the general practice is to use wax with color as the foundation for coating the paper. If Prussian blue is used as a pigment for carbon-paper inks, the blue must be ground so that it is entirely free from grit. The pigments, whether blue, green, purple, or red lakes are ground up into an ink with a suitable proportion of wax and oil. Induline β-base, which is a grayish blue color, not a true lake, is used in both coloring typewriter ribbons and in foundations for carbons. The weighed proportions of ingredients in the ink foundation for carbons will differ according to the type and color of the paper used.

Procedure for Grinding the Dope. The manufacturer of carbon papers makes his own dopes. The color is first introduced in the oil and the color in oil is ground into the melted wax, such as a blend of *carnauba*, *montan*, and *beeswax*. The procedure is to melt the waxes in a steam-jacketed kettle, and then to transfer the melt to a steam-jacketed ointment mill, where the oil and color are added. The grinding between horizontal stones is a slow process and not until the wax-oil color mixture is reground in the same or another mill, does it take on the required homogeneity or luster. The mill is of iron, about 18 inches in diameter, 16 inches in height to the bottom scraper and 29 inches in overall height. It has a corrugated, slightly convex bottom plate which can be enmeshed with the cogs at the bottom periphery of the hopper, and the degree to which this engagement is made determines the flow of the waxy ink between the said bottom plate and the revolving horizontal parallel plate underneath, the ink being removed by a stationary scraper. The ink mixture in the hopper travels by gravity down between the horizontal grinding plates, which are adjusted from coarse to fine grinding by a hand set screw. The drive of the mill can be effected by means of a 2 h.p. motor. The jacket on the mill is suitable for steam pressure up to 40 pounds. The grinding plates can be easily cleaned or replaced by loosening two nuts on the side of the frame. The capacity is about 75 pounds per batch. One mill can be set below another mill, step like, to make the regrinding operation a continuous one.

The colored wax from the mill reaches a temperature of about 200° F, and while warm is run into suitable deep rectangular pans having sloping sides to facilitate removal of the solid wax-ink later. The pans are then sorted until the wax-ink or dope is ready for use, at which time the loaves of dope are removed from the pans, broken up into chunks and placed in a steam jacketed copper vessel which constitutes part of the coating machine equipment. The carbon paper machines will be described later on. The recipes for the wax-inks naturally vary as to whether the carbon papers are for typewriter or pencil copy. The typewriter carbons are mostly in black, but in the "one-time-carbons" blue is used to a considerable extent.

Chlorinated Rubber as Dope Ingredient. The Underwood Elliott-Fischer Co. find chlorinated rubber to be of value as an ingredient of the dope, particularly as a toughening plasticizer. It tends to plasticize the wax contained in the dope in such a way as to render it tougher with the result that the carbons give a sharper imprint. Neidich[94] gives a formula which in actual practice produces typewriter carbon paper giving highly satisfactory reproductions or copies:

	Parts
Petrolatum	42
Carnauba Wax	30
I.G. Wax	10
Chlorinated Rubber	10
Carbon Black	14
Methyl Violet	6
Nigrosine	10

The chlorinated rubber referred to is of the type known under the trade name of "Tornesit." In preparing the dope the waxes and pigments or colors are melted together and the Tornesit is dissolved in toluol, then added to the compound and all are ground together in a hot mill which eliminates the toluol from the formula by evaporation. The completed dope is then ready for use.

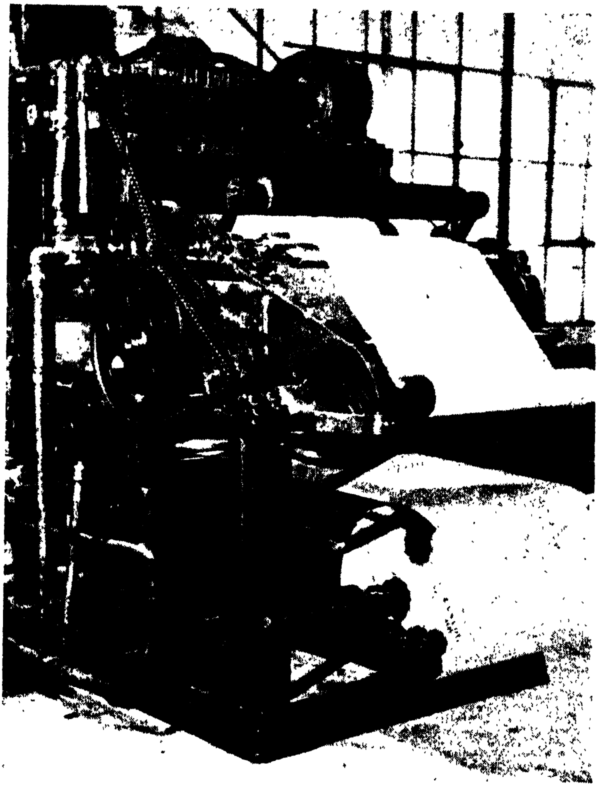


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FIGURE 32. Machine for processing carbon paper. The tissue is fed from the lower roll, passing through the inking mechanism as it is wound on the upper roll. Dual drives on the rolls are necessary to minimize puckering of the paper.

Process of Coating Paper for Carbons. The paper used for manufacturing carbon paper is a special tissue (*e.g.*, loaded and colored) which ranges from 16 to 4 pounds per ream (20 in × 30 in—500 sheets). The usual base weight for typewriter carbons is about 7 pounds. The tissue is supplied by the mills in rolls from 70 to 200 pounds in weight. To-day the latter size is a normal one. The roll is placed in position at the lower end of the machine frame from which it is fed by feeding rollers through tension bars into the coating machine. The tension bars remove wrinkles and puckers. The tissue then passes over rollers, which as they turn, bring the surface of the paper in contact with the melted dope (ink) held in a steam heated fountain. Equalizing devices are provided to lay the ink smoothly, and feeding devices are regulated so as to give a wavy appearance to the coated surface. The equalizing roller, commonly called a jigger, was at one time a brush, but in the improved equipment designed by Mayer[89] in 1911, the jigging roll is a wire bound rod. The size of the wire predetermines the depth of the ink coating. Instead of a piano wire winding on the rod, the rod may have a very light groove cut to the depth of the radius of the wire. Rollers on the machine are of a kind that can either be heated by steam or chilled internally, as needed.

After the ink has been applied the coated sheet is chilled by passing it over a water-cooled roller, and wound up lightly on the receiving drum. According to Olsen[95] a modern machine can process twelve to fourteen miles of carbon paper daily.

When making non-smut, *hard finished carbon paper*, both hot and cold rollers come in contact with the paper. The order of the hot and cold rollers is changed when making *annealed carbon paper* (one side coated) or *double coated paper*. Very light weight tissues are brushed with a jigger to produce *pen carbon papers* and certain typing carbons; brushing gives a notable wave. Carbon papers that are to be gummed into manifolding books are especially prepared with selvedges.

The Mayer coating machine is adaptable to other uses than carbons, such as waxing paper for bread wrappings. Recently it has been employed to apply a hot melt of thermoplastic in a very thin uniform layer to glassine and other papers which are sold for packaging articles to be wrapped and automatically sealed off by a hot iron device.

Lead Pencil Carbons. Lead pencil carbons are made with a cheaper foundation than is used in the typewriter carbon paper. For example, one recipe calls for carbon black 20, mineral oil 140, nigrosine base 3½, *oleic acid* 7, *paraffin wax* 80 parts. The carbon black is first ground with 80 parts of the mineral oil, the nigrosine dissolved in oleic acid added. The hot solution of paraffin with the remaining amount of mineral oil is combined with this mixture and the whole is ground again, before spreading it on the paper at a temperature of about 110° F. In another recipe *carnauba wax*, *montan wax*, and *glyceryl monostearate* are used, the carnauba wax constituting less than 5 per cent of the coating ingredients, whereas in typewriter coatings it is desirable to increase the carnauba wax to as much as 30 per cent.

Stencil Films. Heat resisting stencil films, according to Marran,[86] are prepared by coating cellophane sheet material with a mixture comprising mineral black 5, a non-drying oil 12, a *vegetable wax* 49, and aluminum powder 34 parts.

Master Carbon Sheet for Transfer. In transfer processes for effective reproduction or transfer of designs, drawings, written, and typewritten material from an original master copy, the color constituents of the ink of the carbon paper are transferred to the back of the sheet, forming a reverse copy of the design or writing. In preparing copies from this master sheet, the surface of the copy sheet is moistened with a water-miscible alcoholic liquid, which dissolves the dyes in the reverse carbon paper ink design on the master sheet, thus transferring the original pattern. In general, water-soluble dyes have been used for preparing the carbons, but they tend to soil the fingers of users and to smudge and blur on handling. Brower[15] proposed the use of oil-soluble colors in the carbons, and oil-miscible solvents on the copy paper in the fluid process of transfer from the prepared master copy.

The dyes used by the Brower process are basic azo and amino—azo dyes such as azo-black, the azine dyes, such as the indulines and the nigrosines, or the salts of basic dyes with organic acids, inclusive of nigrosines, indulines, methyl violet base, fuchsine, anthraquinone colors, and chrysoidine. Preference is given to the salts of the higher fatty acids, such as stearates, oleates, palmitates, laurates, and abietates as the sole or principal color constituents in the carbon paper coatings, or transfer inks. Nonaqueous fluid transfer liquids are the lower alcohols, glycol ethers, the lower ketones, acetone, ethyl methyl ketone, and many hydrocarbon and halogenated hydrocarbon solvents. The solvents are applied in the usual manner on a suitable duplicating machine which transfers fluid to applicator roll to dampen the copy paper.

The waxes used for the carbon foundation for a master carbon sheet generally have a melting point above 50 and below 100°, and have in the past been selected from the following: *halogenated naphthalenes, carnauba wax, palm wax, japan wax, montan wax, I.G. wax S*, etc. It is quite probable that the *petroleum ceresins* of low penetration might be effectively used. Modifying agents are selected from a group of alcohols, which includes *cetyl, stearyl, oleyl, palmityl, lauryl* and *myristyl.* These agents lessen the stickiness and tackiness of the dye mixture applied to the carbon paper. Mineral oil is similarly used. A commercial mixture of some of these alcohols—stearyl, oleyl, and palmityl—is known as Stenol. Examples of the foundations are as follows: (a) Nigrosine base N 10, stearic acid 10, stenol 10, and montan wax or Halowax 12 parts. (b) Nigrosine base N 10, stearic acid 10, stenol 10, and carnauba wax 2 parts. (c) Nigrosine base N 10, induline base B 5, spirit-soluble nigrosine jet 10, stearic acid 5, carnauba wax 8, mineral oil 13, and triethanolaminestearate $\frac{1}{2}$, parts.

Wax in Typewriter Ribbons

The manufacture of typewriter ribbons and carbon papers are usually associated. However, there is little in common between the two except that both have a transfer ink and are used on typewriting machines.

Typewriter ribbons are made by inking a closely woven spun silk, rayon, or cotton fabric tape wide enough to produce a number of ribbons when sheared to the specified size. The ink used for charging the ribbons is applied by a brush jigger or porous wiping roll to the tape from ink supplied by a fountain of the inking machine, as the tape is pulled through the feeding rolls at a rapid speed. The tape may be lacquered on the rear side with a coating which is permeable to ink, but prevents excessive flow. The inked tape is then sheared with rotating knives. The ribbons are automatically cut crosswise to metered lengths and spooled.

Ribbon inks are made to a thin paste-like consistency. They consist essentially of pigment ground in a non-drying oil like rapeseed with the addition of an oil-soluble dyestuff, and a water-soluble mineral salt or a glycol ether which can be oil dispersed; the make up of the ink being similar in principle to that of a copying ink. These water-soluble additives permit the use of an increased color-oil ratio and improve the smoothness and fluidity of the paste.

Black ribbon ink is made by grinding lampblack in oil and toning the color with nigrosine and induline bases. Purple ink is made by grinding a methyl violet lake dispersed in oil with a base of methyl crystal violet dissolved in oleic acid. Blue ink is made from a blue lake ground in oil and combined with Victoria blue base dissolved in oleic acid. Red is made from lithol or geranium lake ground in oil. The additives which are sometimes referred to as lustering agents include *Carbowax* as well as some of the glycol ethers. Murphy[92] recently recommended the use of sodium decyl sulfoacetate, sodium monoethyl succinate, and similar compounds to the extent of 0.5 to 2.5 per cent of the concentrated color paste composition. There is an increasing tendency toward incorporating small amounts of resins and synthetic waxes in typewriter ribbon inks to lend both body and luster to the impression.

WAXES IN PHARMACEUTICALS

Waxes are extensively used in pharmaceutical preparations known as cerates and ointments, where they serve as a means of bringing the medicament in intimate contact with the skin. Waxes are also used to some extent in the enteric coatings of pills.

Cerates. The United States Dispensatory defines cerates as "unctuous substances consisting of oil or lard, mixed with wax, spermaceti, or rosin, to which various medicaments are frequently added. The following is quoted *ad verbatim* from this same authority. "Their consistence, which is intermediate between that of 'ointments' and that of 'plasters,' is such that they may be spread at ordinary temperatures upon linen or leather, by means of a spatula, and do not melt or run when applied to the skin.

In preparing them, care should always be taken to select the oil or lard perfectly free from rancidity. In reference to the wax, too, there would seem to be a choice, as experience has shown that cerates made with yellow wax keep longer unchanged than those made with white or bleached wax. . . . The liquefaction should be effected by a very gentle heat, which may be applied by means of a water bath, and during the refrigeration the mixture should be well stirred, and the portions which solidify on the sides of the vessel should be made to mix again with the liquid portion, until the whole assumes the proper consistence, or, as some prefer, the melted cerate is allowed to cool quickly without stirring. When a large quantity is prepared, the mortar or other vessel into which the mixture may be poured for cooling should be previously heated by means of boiling water. It has been proposed to substitute paraffin for wax in the preparation of the cerates, but the great tendency to produce granulation in the finished cerate has largely prevented its use."

Cerates differ somewhat from ointments as primarily the cerate consistency is especially suited for spreading on linen, while that of the ointments is peculiarly adapted to inunction. *Steatinums* have the consistency of cerates but contain a large proportion of tallow. A number of the cerates are, or have been, listed in the United States Pharmacopœia. First is the preparation *Ceratum, U.S.*, or otherwise called *Simple Cerate.* This preparation dates back to 1850. It consists of white beeswax 30, white petrolatum 20, and benzoinated lard 50 parts. For southern climates 5 parts of the latter are replaced by 5 parts of wax so as to hold the consistency. The new U.S.P. XI, gives the simple formula: *white wax* 30, benzoinated lard 70 parts; and cautions to preserve the cerate in a cool place. It is used for dressing blisters, wounds, etc., the object being to prevent contact of the infected region with the air.

Ceratum Camphorae, commonly called "camphor cerate," is composed of camphor linament 10, *white beeswax* 35, white *petrolatum* 15, and benzoinated lard 40 parts. The melt is made of the wax, petrolatum, and lard, and the camphor linament incorporated as the mixture starts to congeal on cooling. It contains 2 per cent of camphor and provides a slightly stimulating dressing. It is not listed in U.S.P. XI.

Ceratum Cantharides, U.S. (Br.), or *cantharides cerate* is prepared from powdered (No. 60) cantharides 35, glacial acetic acid 2.5 (by volume), oil of turpentine 15, *yellow beeswax* 17.5, rosin 17.5, and benzoinated lard 20 parts. The cantharides is moistened with the oil of turpentine and the glacial acetic acid, and set aside in a covered container in a warm place for 48 hours.

Melt the rosin, yellow wax, and lard, strain through muslin, and add the macerated cantharides. Keep mixture in liquid condition on water bath for one hour with occasional stirring. Finally remove it from bath and stir until it begins to congeal. The British method of preparation differs somewhat from the latter. Cantharides cerate is used as a blistering plaster. It is best spread on soft leathers, the skin being first moistened with warm vinegar. The whole art inclusive of blistering cloth, blistering paper, vesicating taffeta, and its application in medicine, is described at length in the United States Dispensatory to which the reader is referred.

Ceratum Plumbi Subacetates or *Goulard's Cerate,* is prepared from lead subacetate 20, *wool-fat* 20, *paraffin* 20, white petrolatum 38, camphor 2 parts. To the melted wool-fat in a warm mortar gradually add the solution of lead acetate, and incorporate it by slow trituration. Add to the mixture the melt of white petrolatum and paraffin in which the camphor has been dissolved; mix thoroughly until homogeneous. The British method is somewhat different. The cerate is used chiefly in excoriations, burns, scalds, and chilblains, and in cutaneous eruptions. Wherever there is an acute active inflammation of the skin it is a most efficient remedy. It is not listed in U.S.P. XI.

Ceratum Resinae, U.S. (Br.) or *Basilicon Ointment,* is made from rosin 35, *yellow beeswax* 15, lard 50 parts. The melt is made and strained through muslin. The British Pharmacopœia prepares it from resin 20, yellow beeswax 20, olive oil 20, and lard 15 parts. The lard and olive oil are added to the previously melted resin and beeswax; the mixture is strained and stirred until cold. Basilicon ointment is much used as a gently stimulating application to blistered surfaces, indolent ulcers, burns, scalds, and chilblains. It has been said that there is no application more efficient in healing ulcers which follows burns.

Ointments. Ointments are unctuous substances softer than the cerates, made to the consistency of butter, so that they may be readily applied to the skin by inunction. When ointments are prepared by merely mixing medicinal substances with simple ointment, *lanolin,* lard, or *petrolatum,* care should be taken if the added substance is a powder, that it be finely sub-divided before being incorporated with the unctuous matter. Ointments often become rancid, and the addition of a little gum benzoin, or a little tincture of poplar buds will arrest the rancidity.

Simple ointment (U.S.P.) is made with *white wax* 5, *wool fat* 5, and *white petrolatum* 90 parts. The ingredients are simply melted together carefully in a suitable dish on a waterbath. The United States and British Pharmacopœias have recognized a number of wax-containing ointments, although some of them have been recently dropped from official recognition. The common rather than the Latin names are given. For the official preparations consult the Pharmacopœia. Examples of these official ointments are: (1) Boric acid ointment: prepared from *wool fat* 5, *white wax* 5, *white petrolatum* 80, and boric acid 10 parts. The boric acid is first dissolved in a little warm water. (2) Rose water ointment: prepared from *spermaceti* 12.5, *white beeswax* 12, oil of almond 56, sodium borate 0.5, stronger rose water 19 parts. This fine cream is really the forebear of all cold creams.

The white petrolatum that is best suited for many cerates, including the ointments, is now obtainable in a form which is somewhat adhesive and has a melting point approaching 55° (130° F), and an outstanding property in its ability to hold oils. A brand of this amorphous-like wax is known as *Protowax*.

Cetyl Alcohol Ointment. Thiele's[120] cetyl alcohol ointment is prepared from *cetyl alcohol* 5, *anhydrous wool fat* 5, *paraffin wax* 15, white petrolatum 50, and liquid petrolatum 30 parts. The waxes and petrolatum are made into an ointment with water in the customary manner of preparing a cold cream. The finished preparation is a beautiful, white, creamy substance which, when applied to the skin, does not look oily and is completely absorbed.

Greaseless Ointments. In recent years attempt have been made to get away from the preparation of ointments from benzoinated lard, petrolatum, lanolin, etc., which are more or less greasy; rather to use greaseless bases employing the technique commonly followed in the preparation of greaseless and vanishing creams. A greaseless base can be made by partially saponifying *stearic acid* with potassium hydroxide, or with triethanolamine, which forms a soap with the excess stearic acid, resulting in a smooth emulsified product. The medicament, however, must be a soluble one; for example, sodium propionate-propionic acid, used to alleviate a disease commonly known as athlete's foot. Many medicaments are not water-soluble, and therefore must still be made of the grease type, or a combination of grease and greaseless base. Instead of stearic acid, *mono-* or *diglycol stearates* have been used, but still more recently the *polyethylene glycols* such as *Carbowax 1500* have met with favor. The latter type of polyethylene glycol dissolves in water to an optically clear solution, has the consistency of petrolatum, and has a melting point equivalent to body temperature. The higher polyethylene glycols have been particularly recommended as a base of a peroxide ointment, since they aid in promoting an even flow of oxygen to the wound.

Wax for Pill Coatings. Enteric coatings for pills—that is coatings which permit pills to pass unaltered through the acid secretions of the stomach but which disintegrate in the intestine—contain wax or waxy substances.[79] Mills measured the efficacy of such coatings, and rated them as follows: cetyl alcohol 81 per cent, cetyl alcohol and shellac 70 per cent, and cetyl alcohol-mastic coatings 97 per cent. The coating solution of the latter type may be made from *cetyl alcohol* 10, mastic 10, and acetone 100 parts.

A timed disintegration, and a new method of applying enteric coatings, was worked out by Worton[133] and his associates. Melt stearic acid 55.5, *carnauba wax* 24.25, and *petrolatum* 1.75 parts; then incorporate powdered agar 13.9, and powdered elm bark 4.6 parts. When cool, grind mixture to a powder. Before applying the powder, the pills and tablets are first treated with a shellac solution, and afterwards dusted with shellac. Heat treatment with an open flame gives a gloss finish and increases the fluid-impermeability of the coating. *Carnauba wax* overcomes the softening of the fatty acid and of the petrolatum. *Glyceryl monostearate* is sometimes used as an enteric coating for tablets. *Magnesium stearate* is used as a dusting medium to prevent pill massing.

In order to protect medicaments in capsules intended to act in the duodenum from being acted upon by the stomach, a coating with stearic acid, m. 65 to 70°, is recommended by Freeman[47]. The capsules are set up on end by means of a suitable holder and dipped into the melted acid at 85 to 90°; then each capsule is reversed and set up on the other end, and again dipped to produce a continuous coating.

WAX IN POLISHES

Polish as an article may be defined as a liquid or pasty substance for giving smoothness and gloss to the surface to which it is applied and rubbed. The field of polishes is a broad one and the polish industry consumes more waxes than any other. The field comprises polishes of the following kinds: abrasive, automobile, buffing, floor, furniture, leather, linoleum, metal, shoe, stove, and miscellaneous others.

Waxes in some form or other are used in most types of polish. Generally speaking, a polish has as its foundation a mass of wax, which consists in part, or as a whole, of a hard wax, one which will impart luster to the surface on which it is rubbed. The preferred polishing wax is *carnauba*- but the carnauba is frequently replaced at least in part by one of the follow, ing waxes: *ouricuri*, *candelilla*, *esparto*, or a hard synthetic, or so-called replacement wax, which latter may or may not contain a porportion of natural waxes. It is customary for the polish manufacturer to combine with the harder wax a less hard and more flexible type of wax, for example one of the following: *beeswax*, *ozocerite*, *refined montan*, *ceresin*, or *petroleum ceresin*; and quite often some *paraffin* as a means of lowering the cost of the wax base. Aside from the floor waxes (see p. 392) most polishes are made up in the form of emulsions, and emulsifiable waxes of the diglyceryl, or diglycol type, are used in addition to carnauba wax or carnauba replacement in the wax mass. So-called rubless floor polishes are of a similar type and these liquids are treated under floor waxes.

When a polish is made for the purpose of cleansing as well as polishing the surface, a mild abrasive such as tripoli becomes an ingredient. A mild abrasive is preferable to a soap as the latter tends to smear. Polishes may be classified into four different types: Abrasive liquid, abrasive paste, non-abrasive liquid and non-abrasive paste.

A polish emulsion is usually prepared in three stages. First, the wax mass is melted. The saponifying solution is prepared separately. Secondly, the heated saponifying solution is added to the molten wax mass with vigorous stirring. Third, turpentine or suitable solvent is added to the emulsion when it has cooled. If abrasive is called for it is added with the saponifying solution.

Automobile Polish. Typical of the polishes is automobile polish. It is made in all four types previously referred to.

Abrasive Liquid Automobile Polish. An abrasive polish in liquid form suited to cleansing and polishing the painted surface as well as the metal trim of an automobile is prepared from an oil and a wax, an organic solvent, water, abrasive, color, and an emulsifying agent to form a more or less permanent emulsion. Certain abrasive liquid polishes have softer waxes or oils blended with a hard wax, such as carnauba; while others have all the polish oil replaced with wax. The abrasive is necessarily a mild one such as tripoli. A small amount of bentonite is sometimes added to aid in the emulsification and to prevent caking or settling of the coloring pigment in the can. As a partial cleaner and as an emulsifier the triethanolamine salt of a fatty acid, *e.g.* triethanolamine stearate, is used, although the trend seems to be towards the use of sulfonated hydrocarbon oils, *e.g.* petroleum sulfonates.

A rubbing wax composition of the aqueous types can be made without the use of soft waxes according to the specifications of Shapiro.[110] A solvent oil is used to replace the soft waxes, thus securing a higher luster from the hard wax. The type of oil is one having a flash point of 140° F, initial boiling point of 360° F minimum, and end point 500° F maximum. The composition is formed by first mixing *carnauba wax* 143, with solvent oil 300 parts, both being heated to 190° F, or somewhat above the melting point of the wax; to this mixture 175 parts of air-flow tripoli are added with thorough agitation; and then oleic acid 55 and solvent oil 300 parts are introduced. During the entire process the mixture is kept at 190° F, and constantly agitated. Finally, triethanolamine (25) is separately dissolved in water, (2300 parts) also kept at 190° F; this solution is intermixed with the general mass and continuously agitated while the balance of the water is added until the total water content has reached 8300 parts. Triethanolamine and oleic acid plus the fatty acids of the wax act as an emulsifying agent to stabilize the emulsion of oily water. The composition is agitated until the temperature drops to 65° F, when it is ready for filling containers.

An automobile polish of the cleaning and polishing type which will leave a bright hard film is one prepared from *carnauba wax* 8, *ouricuri wax* 2, *beeswax* 4, *petroleum ceresin* 3, petrolatum 0.5, naphtha 70, stearic acid 8, triethanolamine (T.E.) 3, water 80, and tripoli 55 parts. The waxes, stearic acid and oil are melted together and naphtha is slowly stirred in. The temperature is maintained at 90–95° (nearly 200° F), and when the solution is clear the tripoli is added, and well mixed in. The water is boiled separately and added while hot with vigorous stirring so as to yield a good emulsion. The stirring is continued until the emulsion has cooled to room temperature; the polish is then ready for packaging.

Material which does not effect polishing or grinding but serves to hold powdering or granular material together is known as a binding agent. In the above formulation, stearic acid and petroleum ceresin are the "binders"; the vegetable waxes the principal "hardeners"; petrolatum the "lubricating agent"; the *amino soap* (T.E.S.) formed by the chemical addition reaction of T.E. to part of the stearic acid the "emollient"; naphtha the "drier"; and tripoli the "abrasive." In a similar formulation of the paste type where about 25 parts of bentonite replace the tripoli, and are stirred into the finished emulsion instead of into the naphtha, the bentonite functions as a milder abrasive, but more particularly as an "adsorbing agent" for the liquid.

The polish is applied by rubbing over the surface well to remove dirt and streaks and then polishing with a dry cloth. In abrasive liquid and paste polishes, both liquid and paste, the abrasives are selected from the following: pumice powder, floated chalk, kieselguhr, koalin, and tripoli. Where soaps are used they must be of the soft kind, such as produced in the making of an emulsion of oleic acid, potassium carbonate, and ammonia water.

Olive Oil Maleic Complex. Clocker[26] found that a certain maleic acid condensation product made an excellent emulsifying agent for the preparation of a liquid auto polish of the abrasive type. To prepare the maleic complex, maleic anhydride is reacted upon linseed, perilla or olive oil, by effecting the condensation in a pressure autoclave at 150° or more. The maleic condensation product is then esterified with the theoretical quantity of an aliphatic or aromatic alcohol to produce an ester with a base to form a soluble salt ester. The resultant product is a water-soluble oil which may be mixed with other oily material to produce an emulsion, superior to sulfonated oil emulsions.

For example, the potassium isoamyl half-ester of the complex may be made as follows: To 50 parts of the viscous oil, obtained by the interaction of 1 mole of maleic anhydride to 1 of olive oil, are added 5 parts of isoamyl alcohol and the ingredients refluxed for one-half hour, to secure the acid ester. The latter is then neutralized by potassium hydroxide. The salt-ester is then added to the water-insoluble ingredients—oil, wax, etc., whereupon the whole may be readily emulsified with water.

Clocker[27] has given the following formula for a very desirable automobile polish: olive oil complex (potassium isoamyl half ester) 10, mineral oil 30, pumice powder 5, amyl alcohol 10, *carnauba wax* 5, and water 40 parts, all by weight.

Abrasive Paste Automobile Polish. The paste type of polish is composed of a suitable blend of waxes and abrasives bound together by a solvent with a suitable water-emulsifying agent. A liquid polish is used as a one-step cleaning and polishing agent, whereas the paste product is sometimes used as a precleaner to a wax application from the non-abrasive liquid type of polish.

A water and abrasive type of polish has been described by Glickman[50] as prepared in three steps: (1) *carnauba, spermaceti,* and *ozocerite waxes* dissolved in naphtha; (2) diatomaceous silica, cream of tripoli, bentonite, color or dye, and water; (3) sodium borate, trisodium phosphate, soap chips of finest grade, and water. The waxes are heated and mixed with the solvent to yield a clear solution. The abrasive, bentonite and color are mixed in warm water and stirred until free from lumps. The alkalies and soap chips are dissolved in boiling water. Then (2) and (3) are thoroughly mixed and the hot wax solution (1) added to the mixture with sufficiently rapid agitation to insure emulsification. The product is then packed warm in suitable containers, glass or metal.

Non-abrasive Liquid Automobile Polish. This type of polish is prepared in much the same manner as the abrasive type, but with the abrasive left out. Many recipes are given in chemical formularies, in which oil, naphtha, wax or waxes, a mild detergent or emulsifying agent and water are the components. One kind is prepared from castor oil, naphtha, alcohol, water, potassium carbonate, spermaceti wax solution, light mineral oil and chip soap. The spermaceti wax solution is prepared by dissolving 1½ pounds of spermaceti in a gallon of naphtha, and then filtering. This type of polish is followed by an application of a wax paste which contains a hard polishing wax.

Non-abrasive Paste Polish. In the manufacture of paste polishes of the non-abrasive type, the selected waxes are melted together. While stirring the wax base the mixed solvents are slowly added. For example, carnauba wax 18, and ozocerite 12, are melted and mixed with 70 parts of mineral solvent; or the 30 parts of wax base might contain 20 per cent of carnauba, 55 of candelilla, 5 of ozocerite, and 20 per cent of paraffin. The solvent might consist of 60 parts of naphtha, and 10 parts of kerosene, the latter to retard drying when the polish is applied; or a little turpentine and pine oil added to the mineral spirits. Utahwax has been used in place of ozocerite, for example, in the formula: Carnauba wax 23, Utahwax bleached 34, paraffin (m. 130° F) 16, and naphtha 160 parts. In some of the softer pastes for automobile, floor, and furniture use, japan wax is utilized in conjunction with *carnauba wax, paraffin,* and *African beeswax.* Certain blends of synthetic resin with wax are said to be useful in improving the gloss and resistance to wear when used in the non-abrasive polishes.

Application of a Finishing Wax. In applying wax to floors, linoleum, furniture and woodwork, certain directions must be followed. All surfaces to be waxed must be free from dust, dirt, grease, etc. Apply a thin, even coat of the wax paste. This can be done conveniently by placing a small quantity of the wax in a double thickness of cheese cloth; apply only the amount which works through the cloth as it is rubbed over the surface, assuring even distribution. Allow the surface to stand until dry (usually 10–15 minutes) and polish with clean rags, a weighted brush, or an electric polisher.

Furniture Polish. Furniture polish at one time was confined to use in polishing wooden furniture. Today it is used to polish both metal and wooden furniture, and differs principally from automobile polish in the absence of abrasives in its ingredients. Furniture polishes are largely non-abrasive liquid polishes, and almost invariably of the water-base formulation. In their preparation a mixture of the softer and harder, or polishing, waxes is preferred. They often contain linseed oil. In general the manufacturers employ an emulsifying base, waxes, mild alkali, turpentine or naphtha, and water. For example, olive oil maleic complex 3, *carnauba wax* 10, sodium borate 2, turpentine 1, and water 90 parts. A polish patented by Shuger[113] comprises mineral spirits 169, light mineral oil 187.5, natural castor oil 93.6, ricinoleic acid 11, water 625, potassium hydroxide solution (1.65 per cent strength) 19.2, and *"Lanette Wax"* 30 parts.

A polish of the emulsion type may be prepared from *carnauba wax* 8, *candelilla wax* 4, *beeswax* 4, *petroleum ceresin* 4, naphtha 70, morpholine 3, stearic acid 8 and water 180 parts. The waxes and stearic acid are melted in a hot water-jacketed kettle, electrostatically grounded for safety. The morpholine is added and then the naphtha very slowly until a clear solution is obtained at about 200° F. The water is brought to a boil and added to the naphtha solution and the whole stirred vigorously by an electrically operated (AC current) stirrer having a large-blade propellor with slow speed. After a good emulsion is obtained the stirring is continued until the product has cooled to room temperature. Morpholine emulsion films are said to become water-resistant within a few hours after application.

A liquid wax finish for wood can be made, according to Bryant,[17] from kauri gum 20, *carnauba wax* 49, and *stearic acid* 31 parts, with seven times their combined weight of turpentine. A patented finish of similar kind consisted of kauri gum 20, *carnauba wax* 31, *beeswax* 18, *stearic acid* 31, and turpentine 700 parts.

Old English Tinted Furniture Wax. Polishes in paste form are made up with wood stains or tints for use on different woods. To illustrate, a "maple tint" is used on Colonial, bleached walnut, bleached mahogany, cherry, beech, ash, golden oak, satinwood, honey maple, etc. A "walnut tint" is used on the different kinds of walnut, Tudor oak, and Feudal oak furniture. A "mahogany tint" is used on the various mahoganies. The object of a tinted finishing wax is to tone down unsightly scratches and nicks in furniture without changing the color of the finish itself. It should also produce a brilliant polish with a light touch of the polishing cloth.

Liquid Stove Polish. A stove polish generally consists of a water dispersion of graphite, a black pigment, wax, resin, and a suitable emulsifying agent. The usual procedure in making liquid stove polish is to melt the waxes together with oil-soluble nigrosine, then thin out with turpentine, and mill in the graphite and lampblack. Graphite is the foundation ingredient which cannot be readily burnt off, whereas the lampblack deepens the color, but burns off readily. The polish must be well rubbed with a soft brush to give a good luster.

A formula given by a manufacturer of *diglycol stearate* for a liquid stove polish is the following: *montan wax crude* 5, rosin 1.5, *paraffin wax* (m. 40–42°) 2.5, *diglycol stearate* 2.5, potassium carbonate 3.5, graphite 50, bone black 20, nigrosine oil-soluble 3, turpentine (or substitute) 97, and water 115 parts by weight. Coumarone resin may be used in place of rosin.

Colloidal clay is sometimes used with the blacks to prevent the polish from caking. *Ozocerite, petroleum ceresin,* and *carnauba waxes* are also sometimes used in stove polishes. What is commonly called "stove blacking" is simply a mixture of graphite, lampblack, rosin and turpentine, and contains no wax.

Buffer Wheel Polishing Compound. A polishing composition suitable for application to buffer wheels is given by Libovitz, *et al.*[80] The composition has sufficient tensile strength to hold together under stringent conditions of use and yet is soft enough to be applied to the surface of a buffer wheel. It also is claimed to polish hard surfaces like steel without undue wear and tear of the buffer wheels used during the polishing operation, and will hold the buffing wheel firm. An example of the polishing compound described consists of silicious earth 1250, aluminum oxide 750, tripoli powder 250, petroleum jelly 250, *ceresin wax* 125, *stearic acid* 50, *montan* 50, tar 25–250, and cotton waste 25–250 parts by weight.

SEALING WAX

Historical. The wax seals used in medieval times were made from resins and *beeswax*. Analyses by Dobbe and Fox of ten seals dating from 1306 to 1504 revealed that all were of this composition. The only deleterious effect of time on these waxes appeared to be a slight absorption of oxygen. The coloring matters used in these seals were found to be verdigris and vermilion.

The modern sealing wax cannot with truth be called a wax, because it is essentially a compound of resins, such as shellac and rosin. The origin of the term "sealing wax" is an ancient one, dating back to the time when colored beeswax was used for sealing letters, and for attaching the impression of seals to documents. Many centuries ago when lac from the East Indies was introduced in Venice the use of beeswax in making sealing wax was discarded. In Spain the lac became known as "Spanish wax" only because of its use in making sealing wax. Gummed envelopes greatly lessened the common use of sealing wax in correspondence.

Kinds of Sealing Wax. Standage[117] attempted a classification of sealing waxes into "extra superfine," "superfine," "fine," and "common," according to the grades of material used. Parcel wax, used for spreading over the strings of packages is of a lower grade, and is made of cheap color such as red lead, and common rosin. Recently sealing waxes have been made in the form of a candle, with a wick, so that a special source of heat for melting the wax is not needed. In these candles the wick is imbedded in paraffin wax, and separated thus from the sealing wax composition, as described by Aktiebolaget Lackljus.[75]

Ingredients of Sealing Waxes. Gum lac, mastic, sandarac and benzoin are used with turpentine in some of the superfine qualities of sealing wax. Perfumed sealing waxes have essential oils and balsams added. Some of the perfuming materials used are pinene, Peruvian balsam, mastic, and musk. An addition of two per cent of benzoin and one per cent of Peruvian balsam, imparts a very agreeable odor to sealing wax. The perfume can be much varied by an admixture of small quantities of oil of peppermint, or bitter oil of almonds. In the finer qualities of sealing wax on the market, the best pale shellac is most often the chief ingredient, while genuine Venice turpentine, magnesia, and a high quality colored pigment form the other constituents. In the lower grades rosin is dissolved in artificial Venice turpentine, and the pigment incorporated. The pigment may be chalk, soot, ocher, or other earth.

Colored Sealing Waxes. In the preparation of a black sealing wax the finer qualities are made with Venice turpentine and shellac in about equal or somewhat greater proportion, and lampblack or boneblack mixed in turpentine added as the pigment. The ordinary black sealing wax is made with shellac, rosin, turpentine, whiting, and lampblack. A deep blue sealing wax made be made from 2⅓ parts of shellac, 1 of Venice turpentine, ⅓ of white rosin, and ⅓ of mineral blue. A very light blue sealing wax may be made from 15 parts of bleached shellac, 35 of gum mastic, 50 of turpentine, 35 of calcined mica, and 25 parts of ultramarine. A very dark blue wax is made from shellac, mastic, calcined mica, Spanish chalk, and cobalt blue.

Gold sealing wax can be made from shellac and turpentine, rosin, mastic, and Dutch gold cut up fine. The color can also be obtained by using 1 part of silver leaf with 6 parts of shellac and one of white rosin. The brown color of the mixed resins imparts a golden tint to the silver. Gold leaf can also be used with chrome green in a wax made of shellac, rosin, and turpentine.

Green sealing wax is made with shellac, rosin, and turpentine, using gypsum, mineral blue and massicot as the pigments. Chrome green and chalk are used in some green sealing waxes. Flake white is used in white, rose, or violet sealing waxes. A rose lake is used to obtain the rose color, and when blended with mineral blue produces a violet color. Yellow sealing wax is pigmented with massicot, or with chrome yellow, which colors can be let down with magnesia rubbed down in turpentine, and incorporated in Venice turpentine, shellac, and rosin.

A recipe by De Keghal[35a] for a high grade red sealing wax is as follows: Melt 7 kg of gum lac at a low heat with constant stirring, and then add successively 5 kg of Venice turpentine, 1 to 2 kg of vermillion, and 70 grams of magnesium carbonate. The latter is added to offset the weight of the heavier vermilion. The mass is stirred vigorously and constantly to prevent the pigment from settling. A small globule is dropped on a glass plate and if color, hardness, and texture prove satisfactory, the flame is lowered to keep the mass just fluid, and 130 grams of Peruvian balsam carefully stirred in. The mass is poured into molds of the desired shape and permitted to cool slowly. The wax is then polished and stamped with a warm stamp.

Brown sealing waxes require for their preparation mixed pigments, such as lampblack and cinnabar, red bole and minium, or brown rotten stone with or without cinnabar. Gypsum and magnesia are used as mineral fillers.

A crimson sealing wax can be made from 2 parts of Venice turpentine, 4 of shellac, 1 of rosin, 1½ of carmine, and 1/10 part of magnesia mixed with oil of turpentine.

Transparent Sealing Waxes. A transparent sealing wax is made from bleached shellac, mastic, and very fine, viscid light colored turpentine. Carefully selected colors may be added if desired. For example, a plain transparent sealing wax can be made from 3 parts of bleached shellac, 6 of mastic, 3 of turpentine, and 2 of chalk. Zinc white may replace part of the mastic and the chalk to obtain a transparent white variety. Finely pulverized leaf metal, gold or silver, can be used for gold or silver transparent sealing waxes. Finally powered yellow or bronze colored mica produce what is known as "aventurine" sealing wax.

Gums used for sealing waxes are selected carefully as to color, and often the original gum is decolorized by melting over a steam bath. If heated over a flame the gum loses some of its plasticity, although this loss can be offset by the Venice turpentine. A good grade of sealing wax should be clear, smooth, brilliant in luster, and should melt without giving off fumes or disagreeable odors. It should not soften so as to fall in drops, and after the impression is made, it should resemble the original wax in appearance. The seal should break easily and without crumbling.

Wax Bottle Seals. A bottle wax is used to bind a stopper to a bottle. In addition it sometimes functions as a tamper proof seal. Since this type of binder is used on spiritous liquors, it is desirable that it be very resistant to alcoholic liquids.

In the manufacture of bottle wax, it is customary to use a considerable amount of pigment, a resin, and a wax. Not all bottle waxes contain resin, and some contain pitch. In order to produce bottle wax at a low cost it is advantageous to use rosin, or to use waste resins as those obtained from the evaporation of the solvent washings of caoutchouc or crude gutta-percha, as proposed by Jasinski.[68]

A black bottle wax can be made by melting together rosin 6½, *beeswax* ½, and ivory black 1½ parts. A softer wax can be made by simply melting *ceresin wax*, and incorporating a considerable amount of lampblack. For spiritous liquors a bottle wax may be made from *beeswax* 1, rosin 2, and pitch 2 parts. For the application of the wax, the neck of the bottle is dipped in the compound and turned horizontally. Red ocher, Berlin blue, and zinc chromate can be used as pigments to obtain red, blue, or yellow bottle waxes.

A bottle wax, according to Braude[14] may be prepared from *carnauba wax* 30, *beeswax* 20, *paraffin wax* (m. 50–52°) 20, whiting 4, barytes 10, and chrome orange 16 parts. The waxes are simply melted together and the pigments stirred in.

An asphalt sealing wax of Hughes[63] is made from asphalt 60, blown asphaltic base oil residuum 16, resin 14, *white wax* 5, and manganese dioxide 5 parts.

Miscellaneous Sealing Wax Uses

Grafting Wax. Grafting wax is a wax used for grafting a limb of one kind of a tree to that of another. It must be tough, resistant to insect attack and weather. The wax is not unlike that of a black bottle wax. A recipe calls for *beeswax* 2, linseed oil 1, rosin 10, and powdered charcoal 1 part. The latter can be replaced in whole or in part by fuller's earth. A grafting wax for small plants can be made by melting together rosin with an equivalent amount of waxes comprising *wool wax*, *beeswax*, and *paraffin wax*, and a sufficient amount of kidney rosin oil is added to the melt to thin the composition when it is poured into cans.

Wax for Desiccators. A mixture of 3 parts of beeswax and 2 parts of petroleum jelly is recommended for making a perfect seal between the body and top of a glass desiccator.

Embedding Composition. Embedding material for micrŏbiological work may be prepared from *paraffin* 200, *rubber* 2, and 0.5 part *beeswax*. The rubber used can be prepared by air drying concentrated latex such as "Heavatex" in thin layers, and then cutting it into small pieces. The wax ingredients are melted together but the added rubber takes a number of hours to dissolve and is stirred occasionally. *Sealz wax* is simpler to use, as it has the rubber in combination with wax; about 10 parts of Sealz wax will replace 2 parts of rubber in the recipe.

Where a specimen is to be examined for its cell structure it is customary to embed the specimen in paraffin, and then slice the whole into the tissue thickness desired by means of a microtome knife. Paraffin has the disadvantage of rolling up into a coil as it is cut. An amorphoid wax, such as a white petroleum ceresin wax m. 160° F will stay flat when cut by the microtome knife.

Waxing Thread. A waxing composition for use on threads and yarns, according to Houston[60] can be made from *paraffin* 16, *cocoa butter* $\frac{1}{2}$–1 and *sperm oil* $\frac{1}{4}$–$\frac{1}{2}$ parts.

Tree Wax Emulsion. Dutton[38a] describes a wax emulsion which will protect living trees from sunscald, borer, and fungus injury, by treating the trunk and branches of the tree. The emulsion is aqueous and comprises paraffin wax, an ammonium salt of a drying oil acid, a colloidal earth, and finely divided aluminum. Waxes, other than paraffin, such as beeswax or carnauba can be employed. An example of the emulsion is as follows: *ammonium linoleate* (dissolved in 50 parts of hot water) 3, bentonite (smoothly dispersed in 50 parts of water) 3, *paraffin wax* 10 parts. The ammonium linoleate solution and the bentonite dispersion are mixed at 70–90°, and the molten paraffin wax slowly poured into the hot mixture; the resulting slurry is vigorously stirred until a good emulsion is obtained. When cooled the product is a creamy stock emulsion. A recipe for spraying is given as: stock emulsion 36, water 36, aluminum powder 7, water to complete 44, parts.

Cordray[29] devised a tree wax for protecting and healing abrasions of trees, which may be prepared from pine resin, *beeswax*, tallow, lime and cottonseed oil.

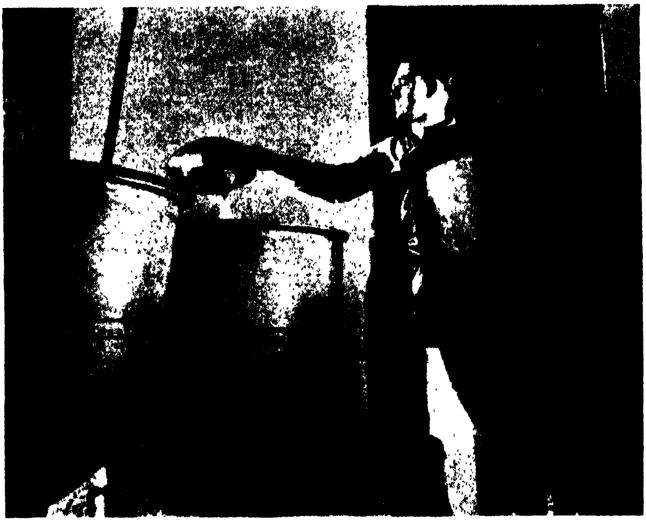
WAX IN SHOE CREAMS

Shoe Creams are paste-wax polishes that may be applied to shoes or leather goods and rubbed to a high finish with a soft brush or polishing cloth. Combinations of different waxes are used in shoe cream formulations. The waxes are referred to as "hard" and "soft." This classification today seems to be based more upon their characteristics as to absorptive capacity of solvent, solvent retention, setting up value, body, consistency, film thickness, rapidity of drying and shining, and keeping quality in the tins, than upon the actual hardness of the wax. In the "hard" classification are carnauba wax, hard paraffin, candelilla, shellac wax, and refined montan wax; and the "soft" waxes comprise crude montan wax, beeswax, ozocerite, and japan wax. In the making of a shoe cream it is necessary to build up a wax foundation in which the hard and soft waxes are properly proportioned.

In the formulation of a shoe cream, attention is particularly given to the individual characteristics of a component wax. *E.g.*, montan wax has a good binding power for solvent, carnauba wax has one of the worst; ozocerite and paraffin have excellent solvent retention power; carnauba wax gives the highest polishing, that is higher than shellac, candelilla, and synthetic waxes. Waxes from the family of grasses, such as esparto, and the hulls of broom corn *Andropogon sorghum*, Brotere, var. *vulgaris* (particularly that of the Western Blackhull Kafir grown in the United States) might do quite as well as carnauba in the shoe cream formulations, if they were available.

Turpentine is the best solvent for the mixed waxes, but turpentine substitutes within the boiling range of 130 to 190° are generally used to thin out the 1 : 1 mixture of wax and turpentine to the consistency desired. In formulations such substitutes are referred to as white spirits, Stoddard's solvent, benzine, or Varsol. The general procedure in making a shoe cream is to melt the hard wax in the boiler, add a solubilized color (*e.g.*, nigrosine base processed with raw montan wax and olein), mix and stir in the soft waxes which have been melted together separately. The turpentine is added at a temperature of 80°, completing the thinning with Stoddard's solvent, benzine, or tetrolin. The temperature is permitted to drop to 48–52° for filling in the tins.

Some creams on the market have shown serious faults, such as incrustations developing on the surface, sweating of the cream sufficient to corrode the tin, granulations throughout, and shrinkage sufficient to make the cream rattle in the tin. These defects result either from lack of experience or carelessness in their manufacture or from a deliberate cheapening by using inferior ingredients or attempting to shorten the length of time required to produce a good product. When a tin is opened the surface should have a mirror finish, and not a veiled bloom, and the cream should retain its consistency over a prolonged period of use. The proportion of soft to hard waxes, the kind and proportions of the solvent, the filling temperature, the degree of chilling, and the temperature of storage of tinned cream, are important factors that must be carefully considered in marketing shoe creams



From: Oilways (January, 1937)

FIGURE 33. In the preparation of shoe creams, the waxes are melted in the double-jacketed steam kettle and the processed color added.

Black Shoe Cream. The formulations of shoe cream given below are those of German manufacture:

(A) I.G. Wax OP 8, carnauba wax 25, raw montan wax (Riebeck) 6, candelilla wax 8, nigrosine base 6 prepared with raw montan wax (and olein) 18, and paraffin m. 50/52° 29 parts. Total 100 parts. The proportion of wax foundation to solvent in the cream is 1 : 2.5 to 3.5.

(B) Carnauba wax 11, raw montan wax 20, shellac wax 16, double refined montan wax 4, nigrosine base 5 with stearin 10, ozocerite 2, and paraffin m. 50/52° 32 parts. The proportion of wax to solvent is 1 : 3 to 4.

(C) I.G. Wax OP 20, shellac wax 22, nigrosine base 3 with raw montan wax (and olein) 9, ozocerite 3, and paraffin m. 50/52° 43 parts. The proportion of wax to solvent is 1 : 2.5.

(D) Carnauba wax 6, raw montan wax 33, shellac wax 4, yellow beeswax 3, nigrosine base 3.3 with stearin 6.7, paraffin 50/52° 44 parts. The proportion of wax to solvent is 1 : 2.5 to 3.

The following are formulations that have been suggested for American shoe creams:

(E) Crude montan wax 32, carnauba wax 25, ebony Utahwax 3, paraffin flakes 55, processed nigrosine 11, and turpentine 300 parts.

(F) Crude montan wax 22, carnauba wax 22, stearic acid 8, nigrosine black 4, ceresin 60, and turpentine 360 parts. The waxes are melted together, and the stearic acid and nigrosine stirred in. The mixture is cooled to about 40° before pouring it into the tins.

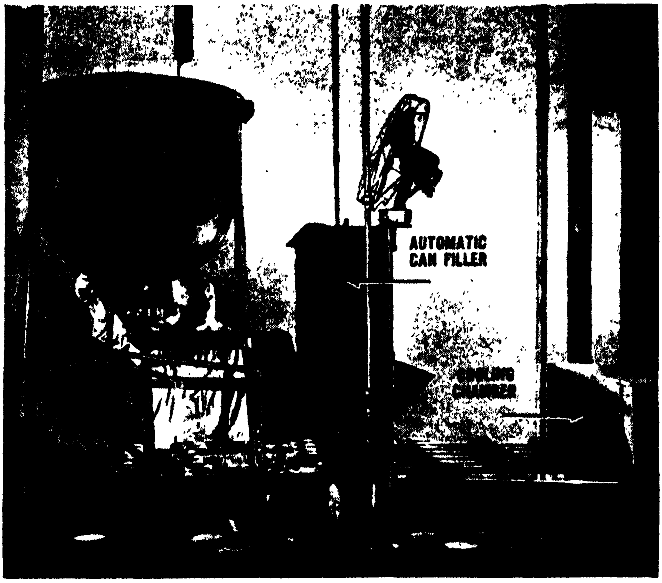
The vehicle most used in shoe creams is turpentine of 310–319° F boiling point. "Stoddard's Solvent," which is a dry cleaner's naphtha, is extensively used. It has a boiling range of 300–410° F. Tetrolin is used mostly in Europe where turpentine is not readily available. Kerosene (boiling point 350–416° F) is also sometimes used in conjunction with turpentine.

Goldreich[53] specifies a polish for boots, leather articles, etc. which has both waterproofing and preserving action, as preparable from gilsonite, *esparto wax*, or *candelilla wax*, turpentine, and oil of mirbane as an odorant. Odorants for shoe polish are nitrobenzene, trichlorobenzene, and ortho-dichlorobenzene. The latter two are added in quantities of ½ of one per cent. The dyes added range from 1 to 3 per cent.

Water Cream Polishes. In the water cream polishes, water is used in conjunction with turpentine and an emulsifying agent, commonly a sodium or potassium soap. The waxes are melted and the organic solvent added while stirring. Water is brought to a boil in a separate kettle, the soap dissolved in it, and the wax-solvent mixture poured into the boiling water, with vigorous stirring. An example is given in a recipe by Davidsohn[33]: *carnauba wax* 10, *beeswax* 3, *paraffin wax* 10, potassium soap 3, turpentine 15, "Stoddard's Solvent" 12, and water 47 parts.

A light neutral water-containing cream polish can be prepared by heating together triethanolamine stearate 25, *beeswax* 10, *candelilla wax* 30, *carnauba wax* 40, turpentine 20, and water 50 parts. The melt is made at 200° F and poured slowly into the hot water at the same temperature, stirring vigorously. If a colored shoe cream is desired, some oil-soluble dye is stirred in the wax mixture while the latter is melting. Shoe creams for white leather contain about eight per cent of zinc oxide. Titanium oxide is also being used as a whitening agent in such polishes.

White Shoe Cleaning Paste. This type of paste may be prepared from titanium oxide 5, lithopone 40, dextrin 6, borax 1, water 48, *candelilla wax* 2 parts, and a little bluing. The wax must be melted in the hot borax solution, the dextrin added, and the pigments added last. This paste can be pressed into tubes. Many of the water cream polishes employ potassium carbonate and rosin as the emulsifying agent to disperse the waxes in water. Clocker[27] gives a formula for shoe cream of the water base type in which a maleic complex is used as a permanent emulsifying agent. The nature of the maleic complex is described on p. 456. The formula is given in parts by weight: olive oil maleic complex 5, *carnauba wax* 6, *candelilla wax* 3, *ceresin wax* 3, turpentine 5, lemongrass oil 0.5, light mineral oil 1, and water 100 parts. Total 123.5 parts.

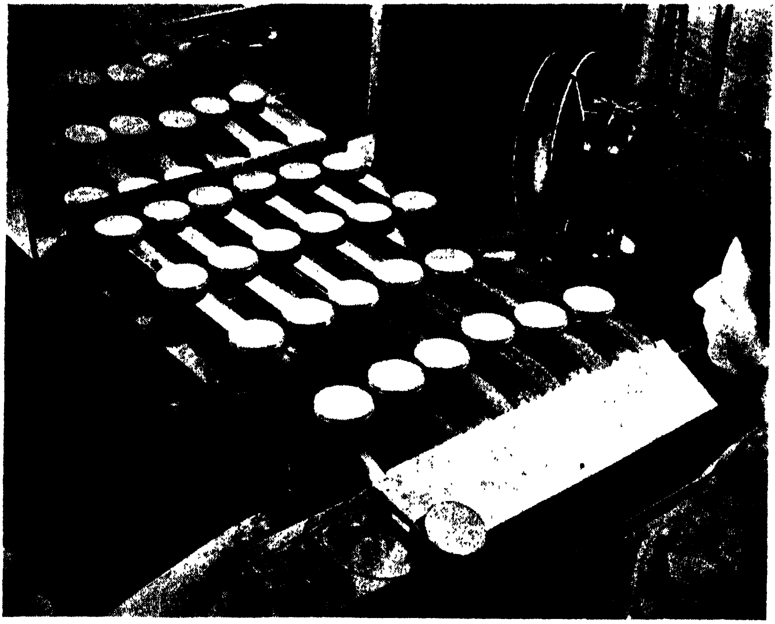


From: Oilways (January, 1947)

FIGURE 34. The shoe cream, fluid at 125° F, flows from the kettle to the automatic can filler, and the filled tins are conveyed through the cooling chamber.

Method of Packaging Shoe Creams. In factory production of shoe creams, also referred to as paste wax polishes, filling machines are employed, and whole rows of flat round tins of 1½ to 2 ounces capacity, are filled on a conveyor belt which runs through a cooling tunnel employing an air current to aid the setting. The filling is by means of a tube or funnel that is automatically inserted close to the bottom of the container and then carefully withdrawn to avoid bubbles and cause irregularities in the surface. After cooling the lids are mechanically applied. The appearance of the shoe cream on opening is often judged by a characteristic of surface ring formation and gloss which comes about through the use of carnauba wax with an appropriate solvent, and is much desired. This feature is enhanced by the use of artificially chilled air in the cooling, although any extreme chilling must be avoided. The filling operation is best carried out in an air conditioned room, but in the absence of air conditioning equipment it is important to exhaust the fumes by suitable exhaust fans.

If the cream is packaged in tubes a softer cream is prepared for the tube filling machine.



From: Oilways (January, 1947)

FIGURE 35. The appearance of the shoe cream is judged by the surface ring formation and gloss. The uncapped tins are inspected through a mirror.

Brown Shoe Cream. Brown shoe cream can be prepared from *carnauba*, *candelilla*, *ozocerite*, and *paraffin waxes*, with oil-soluble brown, and turpentine. The water-paste type employs *diglycol stearate* and powdered soap for dispersion and emulsification of the waxes.

WAX IN SOUND RECORDS

The Early Use of Wax in Sound Records. Under the term "sound records" we include both recorders and reproducers of the phonograph and gramophone type. A gramophone is an instrument for reproducing sound by transmitting to the air the mechanical vibrations of a stylus in contact with a sinuous groove in a moving record. Wax is used in the wax-cylinder phonograph of Edison, and in the making of the recorders of the improved flat record type of Berliner. Originally a glass disc was covered with a semi-fluid coating of ink or paint, in which the stylus cut a sinuous spiral running from the outer edge of the record to the center, or vice versa. A turntable carried the record disc, and was rotated by suitable means. Berliner's next step was to make a record in a solid material by direct etching. A disc or cylinder of zinc or glass was coated with *beeswax* dissolved in benzine. Beeswax was selected because it offered little resistance to the moving stylus and withstood the chemical action of the etching acids. When the recording stylus had traced out its line on the record, and exposed the solid disc below, the latter was etched and a permanent record produced. Copies could be made by the galvano-plastic process, by making a matrix, and impressing the discs of hard rubber or the like.

Sound Record Compositions. Improvements are continually being made in the working out of details in the art of sound record and reproducing. Instead of plain beeswax, compounds of various waxes are used in producing the recording wax; for example, *ceresin*, *carnauba*, *candelilla*, *I.G. Wax*, *paraffin*, and *microcrystalline petroleum waxes*, as well as beeswax. Wax of some kind is also included in formulations of the compounds used in producing the talking machine or reproduction records. A composition suitable for use in making sound records is given as paraffin wax mixed with hydrogenated castor oil, and a suitable filler, such as barium sulfate or clay. Ellis[41, 42] refers to the use of *stearic acid*, asphalt, pitch, talc, etc., as sound record composition ingredients.

Phonograph records have been made from a composition of powdered slate, thermosetting resin, gas black, pitch, with two per cent each of *calcium stearate* and *montan wax*. Gramophone records may be made from a laminated paper material impregnated and surfaced with a composition of shellac, resin, a hard wax, and acetylene black. The discs when molded have considerable strength and flexibility.

A composition for sound recording is given by Schuh,[108] in which *stearic acid* 60, *montan wax* 13, sodium carbonate 5, basic lead carbonate 8, and a plasticizer such as methyl abietate 14 parts, are compounded together.

Treatment of Sound Record Surfaces. Wax surfaces for preparing gramophone matrices may be silvered chemically or sputtered with gold or silver before electrolytical deposition of the copper to form the master shells, according to a process outlined by Majumdar.[85]

Resurfacing of phonograph records is effected by wiping the phonograph cylinders with a solvent such as kerosene, and then wiping the record with a mixture of alcohol, ether and vinegar, so that the record tracing is entirely obliterated.

Method of Reproducing Flat Records. A sound record is originally made in wax, *e.g.*, a compound of *ceresin*, *beeswax*, and *carnauba wax*; a reverse is molded from it in clay or plaster; a copy of the original is molded from the clay or plaster in more durable material such as type metal; a steel negative is pantographed from the latter and a thin sheet of metal is pressed into the steel copy. If desired, the clay reverse may be hardened by firing, and used as a working basis for forming records, as suggested by Head.[59]

In the production of phonograph records the original recording is made in a wax blank, is then coated with a metallizing powder, and subsequently electroplated with a suitable metallic deposit, which after being removed from the wax and backed up by copper serves as a master matrix. The metallizing powder is necessary to make the surface of the wax electro-conductive. These powders are made of an alloy of 90 per cent copper and 10 per cent zinc, the tackiness of the alloy powder being aided by the addition of about 0.1 per cent of *stearic acid* as suggested by Hunter.[64]

Molded sound records for reproduction, as on talking machines, are formed with a hard surface material capable of softening slightly when heated; *e.g.*, a phenolic condensation product, a backing material more plastic when heated than the surface material, and a sheet of fabric between the surface and backing materials. The backing may be formed of wood flour and an equivalent amount of fusible phenolic condensation product or shellac or rosin, as described by Aylsworth.[6] Gramophone disc records are formed of finely ground wood, with or without the addition of flock or shoddy, and binding material such as shellac. The dry material is jigged to produce a level surface, is dampened by steam, and slightly compressed to form a disc, which is dried and subjected to a higher pressure in a hydraulic press, as described by Millar.[91] Coloring matter may be added to the composition, such as azine, induline or nigrosine. A binder of shellac-like composition can be prepared by combining copal resins with polyhydroxy fatty acids, *e.g.*, trihydroxystearic acid, dihydroxystearic acid, dihydroxypalmitic acid, etc.

WAX IN PRINTING INKS, PAINT MATERIAL AND VARNISHES

Printing Inks

For convenience printing inks may be divided into classes: (1) typographic, (2) lithographic, (3) intaglio. Typographic printing includes all the processes of printing from raised characters or plates. Lithographic printing is the printing from a slightly etched stone. Since the printing from flat surfaces has been extended to slightly etched metal plates, the term "planographic" is now used to cover offset lithography, dry offset printing, and offset tin printing, as well as stone lithography. Intaglio printing may be defined as the process of printing from engraved surfaces, such as engraved copper and steel plates, and it includes rotogravure.

Typographic Inks (Ordinary). Typographic inks are used for newspapers and magazines, and are most often black in color. High quality inks for depressed surface plates (intaglio printing) are preferable for advertising displays and for the rotogravure process. In general, tin printing inks are made from pigment, linseed oil, varnish, and metallic drier. Typographic inks for newpaper printing often employ the less expensive higher quality inks.

It occasionally becomes necessary to modify the properties of such inks by the addition of compounds. The latter are referred to as "ink compounds," and comprise one or more combining materials consisting of waxes, soaps, greases, and oils. The purpose of these ink compounds is to improve the working and setting qualities of the inks, and to eliminate such troubles as offsetting, sticking, and picking. The action of compounds seems to be mainly colloidal in nature in that they tend to break the gel formation of the varnishes by reducing their cohesion and adhesion. They also act as emulsifying and dispersing agents, tending to prevent flocculation or agglomeration of the pigment particles.

Common hard soap has been used in inks but has fallen into disfavor because of the difficulty of properly incorporating it in the inks. Grease, such as soap suspended in mineral oil is easily incorporated in an ink, but is apt to leave fat stains on the paper. *Wool wax* or *lanolin* is a suitable compounding material since it is emulsifiable and readily dissolved by naphtha and other common solvents. When added to ink it makes the ink[6] "long," and it tends to improve the lifting and working qualities of inks which have pigments of low oil absorption or high specific gravity. Its principal use, however, is in its combination with either *paraffin* or *beeswax* as a non-crystallizing compound for use in first color, opaque, process yellows. Woolwax has the power to hold small quantities of paraffin or beeswax in suspension, thus preventing them from crystallizing out of the inks and causing an undesirable graininess. The paraffin or beeswax should be melted with the wool wax or wool grease, cooled and then given a run over the mill before the compound is introduced into the inks. Tallow is also sometimes used in printing inks.

Beeswax is a common ingredient of non-offsetting and non-crystallizing compounds. According to Wolfe[130] it produces a somewhat less grainy compound in general than does *paraffin wax,* and possesses better working and gripping qualities. The incorporation of from one-half to one ounce of beeswax to the pound of ink by melting and grinding will enable the ink to be printed on top of a crystallized color without crawling. The inclusion of a small percentage of *lead oleate* or paste drier along with the beeswax will increase the grip of the ink on the dried surface and improve its drying quality. Beeswax facilitates clean printing on an "offset" printing press.

In the line of mineral waxes *paraffin*, *montan*, and *ozocerite*, are the important ones to the ink maker. Paraffin is usually employed in conjunction with another wax, since if used alone it is apt to crystallize out. *Montan wax* is finding a constantly increasing field of application as a substitute for *carnauba wax* in the preparation of ink compounds. Wolfe[130] states that it is possible to incorporate more of it into a given ink than carnauba. The use of *carnauba wax* in a bronze printing ink is described in the following recipe by Mason: polymerized tung oil (240°–280°) 37, linseed oil (boiled) 19, carnauba wax (refined) 4, turpentine (spirits) 7, and bronze powder 33 parts. In the formulation of the bronze ink the boiled linseed oil is added to the polymerized tung oil and the mixture is kept at 200° for two hours, during which time the wax can be melted in and dispersed by stirring. After cooling the bronze powder is moistened with the turpentine and stirred in before milling for smoothness and uniformity.

Ozocerite is superior to paraffin for use in printing inks since it will not crystallize, and the addition of 25 per cent or more of ozocerite to paraffin will prevent paraffin from crystallizing. Ozocerite is, however, an expensive wax to use. In general it retards the drying of inks and reduces their tack. *Petroleum ceresin waxes* are cheaper and have a similar field in printing inks.

Petrolatum itself finds a wide application as a reducer, extender, and cheapener in the manufacture of colored perfecting press, poster, and show card inks. An ink for printing cellulose and cellophane is made from titanium oxide 63, long oil varnish 6, lithographic oil 29, paraffin in petrolatum 2 parts. The latter is made by melting 6 parts of *paraffin* in 94 parts of *petrolatum*. The varnish is made by heating 10 parts of an alkyd resin with 750 parts of tung oil for an hour. The ink is said to adhere to cellophane and be tack-free in four hours.

Process Inks (Typographic). By properly combining, or superimposing the three so-called primary colors, red, yellow, and blue, practically any color may be reproduced. This is the fundamental principle upon which three-color process printing is based. Halftone plates are made from negatives of pictures taken with a camera using color filters. The manufacturer of process inks requires closer control of the physical characteristics than any other type of printing ink. The second color should be less tacky than the first color, and the third color less tacky than the second. Wolfe[130] gives the following recipes for the process inks.

Process Transparent Yellow. No. 00 transparent litho varnish 25, No. 1 transparent litho varnish 15, soft wax compound 6, paste drier 4, quinoline yellow lake on hydrate base—dry 50 parts by weight.

Process Blue. No. 00 transparent litho varnish 36, No. 1 transparent varnish 11, cobalt drier 6, soft wax compound 5, phosphotungstated Victoria blue toner, dry 1, Peacock blue lake on hydrate base, dry 41 parts.

Process Red. No. 00 transparent varnish 20, No. 1 transparent varnish 15, soft wax compound 5, paste drier, 5, phloxine toner, dry 25, aluminum toner, dry 25, aluminum hydrate dry 30 parts. The soft wax compound can be made up with neutral wool grease, or *lanolin,* in combination with *paraffin* or *beeswax* and lanolin should be melted together, cooled, and then given a run over the mill before the compound is introduced into the inks. Wool grease is also especially valuable in inks that contain considerable proportions of pigments of low oil absorption or high specific gravity, as it tends to improve their lifting and working qualities.

Lithographic Inks. A small percentage of tallow and *wax compound* is often added to lithographic inks to make them more water repellent so that they will resist the action of the dampening solutions more completely. The compound also aids the working of the ink by slightly reducing the tack. Two per cent of the usual compound is ordinarily sufficient for this purpose. In offset lithographic printing the waterproof ink is transferred by a dampened roll to the etched metal plate and from there to a revolving cylinder covered with a rubber blanket and thus on to the sheet to be printed, *e.g.* paper or tin plate. Waxes are only occasionally used in the offset T.P. (tin printing) inks. *Wool grease,* however, is used in dry offset printing inks for printing tinted backgrounds for checks, labels, etc. A little wax compound added to the ink improves its working qualities. Dry offset inks need not be waterproof. Japan wax may be used in dry offset inks.

A typical lithographing ink for carboard, in which ink *wool wax* is used, comprises: *wool wax* 2, spindle oil 1, heavy lubricating oil 42, water 45, carbon black 8, induline 0.8, and red oil 1.2 parts. The spindle oil is warmed with the wool wax; the induline is ground with the red oil. The wool wax solution is mixed with the lubricating oil and water added next. When smoothly emulsified the carbon black and ground color are stirred in and the mixture is milled.

Intaglio Printing Inks. Under this heading are many kinds of ink for (*a*) copper plate engraving, (*b*) steel plate engraving, (*c*) stamping, (*d*) photogravure, (*e*) rotary photogravure, (*f*) thermographic processes. Waxes are seldom used in the intaglio printing inks, except in the so-called "transfer inks," which are used on the base paper material prior to printing the design.

Transfer Inks. In intaglio printing, certain types of waxes have been employed in treating temporary transfer bases prior to printing of the design. Wade,[124] impregnated a sheet of thin paper with paraffin for pressure transfer, and the pattern was placed on the wax with ink containing a non-drying oil (castor). Foundation materials for transfer inks may include rosin with the wax. The rosin is sometimes substituted for by paracoumarone; *e.g.*, a composite of *Chinese insect wax* and paracoumarone can be used to coat glassine paper, and a design effectively placed on this with a nitrocellulose metallic powder marking compound. Shellac sizing is subsequently added to the print. For some purposes, instead of printing the design on a wax coating, the pattern is stamped out from a cellulose ester film, and attached to the waxed surface by means of gum damar or other suitable adhesive.

Gravure Printing Thermo-fluid Inks. For large volume high speed printing, by gravure, letter press, or offset, of containers, publications and literature of all sorts, Huber[62] invented a type of printing ink which is normally solid but which becomes fluid when used with a heated letter press, litho and/or gravure printing machine. The ink is heated to an elevated temperature at which it is molten and possesses a suitable printing consistency. A printing effect is obtained in which there is no penetration to the fibers, with resultant clarity and sharpness of outline of the printed ink films. An example of a composition of the fusible ink is given by Huber as carbon black 10, gilsonite 45, *candelilla wax* 45 parts. The wax is first melted and the carbon black thoroughly incorporated into the wax by use of mixing and milling equipment, after which the gilsonite may be added in a steam jacketed mixer. The ink softens at about 64°, and prints well at 75°. A more complex composition is given as gilsonite 50, *candelilla wax* 40, chrome orange 6, No. 3 litho varnish 3, and carbon black 1 parts. Blends of *candelilla wax* and gilsonite have the property of wetting and adhering to the fiber of the stock. Another sample is "Santo Resin" 60, *ozocerite* 20, and peacock blue 20 parts. "Santo Resin" is the isobutylene polymer of the the Monsanto Chemical Company. It melts at 104°. A rotary letterpress ink suitable for the printing of magazines is as follows: Cumar V resin 30, gilsonite resin 30, china wood oil (heavy bodied) 20, *carnauba wax* 20, carbon black 9, and toners 2 parts. This ink melts at 78°, is liquid at 85°, and has a suitable printing consistency at about 100°.

In the gravure printing with thermo-fluid inks the etched plates do not require deeply etched cells, and the etchings are best made up shallower than customary for the wet inks. The press is equipped with suitable heating means to maintain the ink in a proper liquid condition during the printing operation.

Electrotype Impressions. When it is desirable to produce several plates from the original type or linotype slugs, a process known as electrotyping is employed. In the electrotyping process, as in stereotyping, an impression of the surface is made, using wax as a medium, although resinous compositions and lead also are utilized. For the wax the most suitable medium is *ozocerite*. In the absence of European ozocerite, both South American and Utah ozocerites have been successfully used. *Beeswax* is also used for the purpose and may be admixed with the ozocerite. The impressed mold is made conductive by a coating of graphite. The wax and resinous molds are then treated with aqueous copper sulfate and iron to form a thin coating of copper on the mold. Subsequently a layer of copper is deposited upon the surface electrolytically, resulting in a metallic sheet whose surface corresponds to that of the type from which the impression was taken.

Wax in Varnishes

Waxes are used to some extent in both air-drying and heat-drying varnishes. In air-drying varnishes they can only be used in minute quantity as they interfere with the drying. Their more extensive use is in the baking varnishes, some of which are referred to as "slip varnishes."

Candelilla wax is incorporated to the extent of about ½ per cent in a varnish for finishing linoleum to a luster. Wax may be used in varnish that is applied to lithographed tin sheets that are oven dried and then fabricated into bottle caps, the wax furnishing the necessary lubrication to the dies of the stamping press so that the work is free from scratches and imperfections that would otherwise result. So-called "Drawline Varnish" has wax incorporated in it. The kind of wax used in a varnish varies with the kind of use to which the varnish is put. High-melting-point waxes such as *carnauba*, *montan*, and the harder *microcrystalline petroleum ceresin* are to be preferred. These waxes bloom to the surface as the varnish film dries. It is customary in the preparation of the varnish to cook the resin and oil together, and add the wax after dropping the temperature, and before adding the naphtha or other reducer to thin, or to add it while thinning.

Waxes such as *paraffin* and *white ceresin* are sometimes incorporated in varnishes to increase the flexibility of the dried film. They are used to the extent of one per cent or less of the non-volatile content for coating papers, etc., without inducing the wax to bloom from the surface coated. An amount of wax exceeding one per cent is incorporated in the varnish when it is desirable to have the wax bloom out on heat drying a varnished surface.

Waterproof Label Varnish. In a varnish for application to absorbent paper labels with inked surfaces a varnish with *paraffin wax* as an ingredient can be advantageously employed. Examples have been given as:

(1) Batavia gum damar 63, tung oil 72, kerosene 33.7, cobalt drier (6%) 417, paraffin wax 1.6 parts. The resin is cooked with the oil to 450° F. The kerosene, drier, and wax are added in order, and the whole allowed to cool. The varnish is colorless and dries with a good gloss.

(2) Batavia gum damar 135, tung oil 135, kerosene 67.5, cobalt drier solution (6%) 30.5, paraffin wax 5.5 parts. The drying time of this varnish is 2½ hours and it dries with a good gloss. This formula has been recommended for a non-absorbent surface.

There are many modifications of these label varnishes. Some with the higher gloss are slower in drying.

Wax in Paint Material

Wax is not extensively used in ordinary paint materials. It does find a use in specialty paints and in the making of bronze powders the waxy property of *stearic acid* is of particular value aside from its negative potential property.

Wax, customarily *slack wax,* is an ingredient of colored coatings made from casein and pigment, used in the coating of gloss papers produced for packaging chocolate candy bars. The paper is double coated with the pigmented coating and receives its gloss by rubbing the coated paper crosswise with a bar of flint by a mechanical reciprocating motion. These polished papers are produced in other colors than chocolate-brown and find an extensive miscellaneous use.

Polishing Paints. For some purposes it is desirable to apply a paint on which a design can be effected by polishing, and which can be washed or scrubbed without removing the design. Gargen and Ernst[49] have invented a paint containing wax for such a purpose. For example one of their paints has the following composition: lithopone 61.5, aluminum silicate 8.8, beeswax 0.4, "flatting varnish" 20.1, and boiled linseed oil 9.2 parts. The amount of wax incorporated, customarily not over 0.5 per cent is the optimum quantity that can be used without getting a waxy or greasy finish which would retard drying and make it difficult to repaint. The wax improves the washability of the painted surface giving a surface which can be cleaned without marring the design. "Flatting varnish" as above referred to is a varnish composed of soya oil 10, tung oil 10, East India gum 15, and mineral spirits 65 parts.

Wax in Aluminum Powder. There is one fundamental way to make metallic bronze powders, and that is to stamp the pieces of aluminum or gold bronze alloy—whichever is desired—so that the metal will flow into flake-like particles, and the pressure will burnish and enhance the luster. As customarily carried out the manufacture resolves itself into a process of hammering aluminum under mechanical stamps, and this requires a suitable lubricant. The best lubricant appears to be *stearic acid.* The stamping of the flake against flake seems to assist shearing the larger flakes into smaller ones. The final operation is a polishing one in a cylindrical drum with a series of brushes bearing lightly against the inner surface. Stearic acid is here again used as the lubricant. Bronze powders are extensively used in paints.

Waterproofing Building Material. There is need for a wax composition that will be useful in the waterproofing and weatherproofing of building materials such as brick, cement, stone, terra cotta, and wood. The composition used must take care of the discoloration that results by the efflorescence of salts dissolved out of the building material. Examples of waterproofing compositions are: Chinawood oil 22, paraffin wax (m. 122° F) 13, japan drier 0.1, solvent naphtha 64.9 parts; or (according to Baldeschweiler[7]) paraffin wax (m. 122° F) 13, cracking oil tar 15, japan drier 0.1, solvent naphtha 65 parts. Coating compositions may be applied by brush or spray.

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Appendix

Tables of Physical Constants of Waxes

Viscosity and Specific Gravity of Waxes at Changing Temperatures

Wax	Temperature (°F)	Viscosity Saybolt Universal (sec)	Specific Gravity T°/15°
Paraffin (S.O.N.J.)	60	—	0.9086
m. 128/130° F	140	50.6	0.8105
	180	42.5	0.7970
	210	39.0	0.7875
	250	36.2	0.7725
Ozocerite (JAA)	180	53.8	0.8120
m. 161° F	220	44.6	0.7965
	250	41.7	0.7870
Beeswax, white	160	119.0	0.8670
m. 148° F	205	73.7	0.8505
	250	54.6	0.8345
Beeswax, yellow	165	103.9	0.8650
No. 2	205	69.4	0.8490
	250	54.0	0.8350
Ceresin, artificial	180	42.1	0.7985
m. 166° F	220	37.9	0.7855
	250	36.3	0.7750
Ozocerite, commercial	170	55.9	0.8120
m. 161° F	210	46.1	0.8010
	240	42.5	0.7870
	250	41.7	0.7840

When the viscosities are plotted against temperatures the resultant curves are parabolic. From such curves the viscosity at any one temperature may be computed. Curves showing the relation between the specific gravities and temperatures above 25° are very nearly straight line curves which tend to break and change their direction at the temperature of solidification of the wax.

Viscosities—Saybolt Universal

Wax	170°	200°	230°	260°	Flow
Paraffin	44.0	39.7	37.0	36.0	fast
Ozocerite	57.0	49.0	44.0	41.6	slow
Beeswax	107.0	77.0	61.0	54.6	sluggish
Ceresin	43.6	39.7	37.0	36.0	fast

Hardness Values of Waxes
(Shore Durometer)

	At 4°	At 25°
Beeswax:		
Refined, ordinary	86	65
Yellow, U.S.P.	75	43
Sun bleached, U.S.P.	87	66[a]
Carnauba wax	100	100
Candelilla wax	100	100
Ceresin:		
Italian white, m. 158° F	75	49
Domestic, m. 185° F	92	69
Cheap artificial	70	32
Artificial, soft for lubricating	89	28
Cranberry wax, raw	100	100
Esparto wax	100	100
"I. G. Wax OP"	100	100
"I. G. Wax Z"	—	94
Japan wax	50	21
Myrtle wax	—	78
Myristic acid (90%)	54	32
Palmitic acid (90%)	—	50
Microcrystalline petroleum waxes:		
Pale yellow, m. 185/190° F, Oklahoma	95	90
"Superla," (S. O. of Indiana)	—	75
"Petrosene A," m. 167/171° F	76	47
White bleached, m. 163/168° F., Oklahoma	78	54
Amber, m. 160/165° F, Oklahoma	77	51½
Montan wax:		
Crude black	100	98
Bleached yy.-white	—	78
"Opalwax No. 10"	100	100
Ouricuri wax	100	100
Ozocerite, pure white	67	53
Palm wax, commercial	100	82[b]
Paraffin wax:		
American, m. 123/125° F	70	50
American, 128/130° F	75	54
American, 138/140° F	—	68
American, 160/163° F	—	82
Asiatic, 128/130° F	85	76
"Pliowax," blend	95	70
"Rezowax A," synthetic	100	100
Shellac wax	97	95
Stearic acid:		
"Neo-Fat" 90% (Armour & Co.)	68	55
Ordinary commercial	84	76
U.S.P.	95	93[c]
Spermaceti	70	49
Sugar-cane wax, Louisiana, refined	100	98
Vegetable fiber wax	—	85

Note: [a] The durometer hardness determinations on five specimens of bleached beeswax were 45, 74, 63, 58, and 65. A similar variation can be found in yellow beeswax. [b] Three specimens of palm wax showed 81, 85 and 80 hardness, or 82 average. [c] U.S.P. grades contain much palmitic acid which tends to increase the hardness.

Penetration Values of Waxes at 25°
(Penetrometer needle No. 14,—5 sec penetration,—100 g top wt.)

Wax	Value (mm × 10)
Beeswax:	
Yellow U.S.P.	17
White U.S.P.	11 –11½
Wild, black	22 –23
Calcium myristate	6¾
Calcium stearate	4
Candelilla wax	1½
Carnauba wax	1
Ceresin wax:	
Italian white, m. 158°	14
Artificial, soft for lubricating	25
Esparto wax	1½
"I. G. Wax":	
Z	1
OP	1¼
OZK	144
Japan wax	62
Montan wax, bleached	9½–10
Myristic acid	23½–24
Myrtle wax	7½
Microcrystalline petroleum waxes:	
"Protowax" (petrolatum type)	217
"Petrowax" (Gulf Refining Co.)	23
"Petrosene A" (Socony Vacuum Oil Co.)	20 –21½
"Gem Yellow"	20 –20½
"Aristowax"	14½
"Be-Square White" Bareco Oil Co.	13 –13½
"Amor 1200 A"	6½– 7¼
"Sp. Hard Amber" (Koster Keunen)	6 –6½
"Pale Yellow" m. 190/195° F (Bareco Oil Co.)	4½– 6½
"Superla Wax, Yellow"	11 –11½
"Opalwax No. 10"	2
Ouricuri wax	1
Ozocerite "JAA"	13
Palmitic acid	7
Paraffin:	
American, m. 128/130° F (S. O. N. J.)	15
American, 128/130° F (Atlantic Refining Co.)	37½
American, m. 138/140° F	15
American, m. 160/163° F	8½–10
Asiatic, m. 148/150° F	12
Asiatic, m. 160/162° F	7
Asiatic, m. 190/195° F (petroleum ceresin)	5
"Rezowax A"	5 – 6
Spermaceti	16
Stearic acid:	
"Neo-Fat 1–65," pure	11
Double pressed	11 –11½
Triple pressed (U.S.P.)	5
Sugar-cane wax, refined Louisiana	2
Vegetable fiber wax	1
Vegetable oils (mixed) hydrogenated	2
"Utahwax"	4

Melting Points of Waxes

	Melting Point (°C)	Melting Point (°F)	Solidifying Point (°C)
Jojoba wax	11.2- 11.8	52.1- 53.2	—
Paraffin scale	35–40	95–104	—
Wool wax	36–42	95–104	30–40
Spermaceti	45–47	113–116.6	42–42.5
Bayberry wax	46.6–48.8	116–120	39–43
Paraffin m. 118/120° F	47.8–48.9	118–120	—
"Lanette Wax"	50	122	—
Chinese coccid wax	50–51		
Japan wax (a)	50.4–51	122.7–123.8	50.8
Parawax	51–58	123.8–131	—
Stearine	52–56	125.6–137.3	50–54
Coccid insect wax (Ceroplastes spp.)	52–58.5	125.6–137.3	—
Paraffin 123/125° F	52.2	126	50.8; cloud pt. 51
Japan wax (b)	52.5–54.5	126.5–130	45.6–46; cloud pt. 40.5–41
Diglycol stearate	53–54	127.4–129.2	—
Paraffin U.S.P.	53.3–54.4	128–130	51.8–52.9
Paraffin m. 128/130° F	55	131	53.4; cloud pt. 53.6
Sugar cane wax, crude	55	131	51
Arjun wax, Indian	55–63	131–145.4	—
"Pliowax"	55.6	132	—
Slop wax, paraffin	55.7–83.3	132–182	—
Gondang wax	56–57	132.8–134.6	51
Glyceryl monostearate	56–57	132.8–134.6	—
Stearic acid, flakes	57.2	135	56.6
Glycowax	58	136.4	—
Paraffin m. 138/140° F	58.9	138	57.4
Ceresins, artificial	59.5–71	139–160	—
Sugar cane wax, East Indian	60–62	140–143.6	—
Ghedda wax	60.4–66.4	140.7–151.5	60
Ozocerite, commercial	61–78	142–172	—
Beeswax, yellow commercial	62–66	143.6–152.8	60.5–63.5
Beeswax, yellow U.S.P.	63–64.2	145.2–147.6	61–63
African beeswax	64–65	147.2–149	61–62
Cotton wax	64–66	147.2–150.8	—
Beeswax, white U.S.P.	64.7	148.5	63.3
Halowaxes	65–130	149–266	—
Candelilla wax	75.8–77.4	150.8–159.8	63.8–67.7
"Karawax"	67–70	152.6–158	—
Petrowax A, microcrystalline hydrocarbon	70	158	67.8
Montan wax, bleached	70–85	158–185	—
"Utahwax," refined	70.4	158.7	70.0
Stearic acid, pure	72.1	161.6	—
"Utahwax," crude	73	163.4	—
Gondang wax	73	163.4	—
Coccid insect waxes, Japanese	73–78	153.4–172.4	—
Rod wax	73.9–80.5	165–170	—
Shellac wax	74–80.8	165.2–177.4	76.6
Esparto wax	75–78	167	69
Petrosene A, microcrystalline hydrocarbon	75.6	168	74.2
Be-Square, white, microcrystalline hydrocarbon	77.2	171	76.7
Sugar cane wax, Louisiana, refined	77.8	172	70.9
Snow brush wax	78–79	172.4–174.2	—
Montan wax, crude	78–85	172.4–185	—
Ouricuri wax, filtered double refined	79	174.2	68

Melting Points of Waxes—(*Continued*)

	Melting Point (°C)	Melting Point (°F)	Solidifying Point (°C)
Pisang wax	79–81	174.2–177.8	—
Fiber wax, refined	81.2	178.2	72.1
Chinese insect wax	81.5–83	178.7–181.4	80–82
Raffia wax	82–83	179.6–181.4	—
Carnauba wax	83–86	181.4–186.8	80–84
Ouricuri wax, crude	83–87	181.4–188.6	72–76
"Rilan Wax"	84–85	183.2–185	—
Palm wax	85–86	185 –186.8	75
"Opalwax"	86–88	186.8–190.4	74.2
"Pale yellow 180," microcrystalline hydrocarbon	87.4	189.3	85.5
Rhimba wax	88	190.4	—
Surakhansk ceresin	89	192.2	87.7
Carnauba substitute, "Norcowax C"	92.9	199.2	69.1
I. G. Wax Z	101–103	214–217	96.5
U. G. Wax OP	105–108	221–226	84.0
Acrowax C, synthetic	140	284	138.6
Cranberry wax, hot solvent extracted	194–217	381–423	—
Santowax P	200–215	392–419	209–213

Table Showing Relation Between Oil Content and Penetration (ASTM D5–25) for Softer Microcrystalline, or Petrolatum Waxes (m. 160–170°F)

Per Cent Oil Content	Penetration Value
3.0	29.0
4.1	33.0
4.6	35.0
5.8	40.0
6.8	45.0
8.0	52.0

Table Showing Relation Between Oil Content and Penetration (ASTM D5–25) for Harder Microcrystalline, or Petroleum Ceresin Waxes (m. 170–180°)

Per Cent Oil Content	Penetration Value
very low	8.5
1.6	10.5
2.2	12.0
3.3	15.0
4.1	17.0
5.1	20.0
6.7	25.0
7.3	27.0
8.0	29.0

Table Showing Relation Between Melting, Solidifying, Softening, and Liquating Points of Various Waxes

Name of Wax	Melting Point (°) (Drop Method)	R. and B. Point (1°/per min.)	Solidifying Point (°)	Softening Point (°)	Liquating Point
Amber 160/165* Microcrystalline	78.9	—	77.1	61.7	none
Aristowax (Union Oil Co. of Calif.)	62.6	—	62.1	—	60.0
Beeswax, yellow refined	64.2	65.0	62.5	48.4	slight indication
Beeswax, yellow U.S.P.	64.2	65.3	62.9	—	none
Beeswax, white	64.7	—	63.3	—	none
Beeswax, Macassar (Batavia)	62.8	—	58.6	—	56.0
"Be-Square White"*	77.2	76.1	76.7	56.7	—
Black Micro Wax 180/190*	89.1	—	86.6	77.0	—
Black Micro Wax 160/165*	77.0	—	—	58.0	—
Candelilla wax	70.6	70.0	66.7	66.9	none
Carnauba wax No. 1	83.0	85.0	82.0	82.0	80.6
Carnauba substitute "Norcowax C"	92.9	—	69.1	74.2	78.3
Ceresin, artificial 150/160 (American Cyanamid)	71.4	57.5	indefinite	35.5	46.7
Esparto wax	78.1	—	68.8	—	65.6
Fiber wax	81.2	—	71.1	—	none
Jojoba wax	11.2–11.8 (capillary)	—	6.7	—	—
Montan wax, crude	87.0	—	77.3	—	none
Opalwax No. 10	87.4	—	74.2	—	none
Ouricuri wax, crude	84.3	—	72.2	—	none
Ouricuri, filtered double refined	79.0	79.0	68.0	72.3	none
Ouricuri, refined flakes	83.3	—	72.9	—	none
Ozocerite, refined	75.0	68.5	64.7	—	none
Pale yellow 180* microcrystalline	87.4	86.1	85.5	72.8	none
Palm wax A, commercial	80.6	—	65.6	—	53.9
Palm wax B, commercial	80.7	—	65.6	—	53.9
Palm wax (Ene)	85.0	—	74.1	—	none
Paraffin m. 123/125° American refined, S.O., (N. J.)	52.2	—	50.8	—	46.9
Paraffin m. 128/130° American refined, S. O., (N. J.)	55.0	56.1	53.4	37.8	—
Paraffin m. 128/130° Asiatic refined, Asiatic Pet. Co.	54.6	—	53.3	—	50.3
Paraffin m. 133/135° Atlantic Refining Co.	56.9	—	55.1	—	51.1
Paraffin m. 138/140° American refined, S. O., (N. J.)	58.9	60.0	57.4	45.0	53.3
Paraffin wax, ceresin, Asiatic	91.0	—	90.0	—	none
Petrosene A, Socony Vacuum Oil Co.	75.6	74.6	74.2	61.1	none
Petrowax, Gulf Refining Co.	70.0	67.5	67.8	49.4	none
Shellac wax	80.8	—	76.6	—	70.0
Stearic acid, U.S.P.	56.1	—	54.2	—	none
Sugar cane wax, Louisiana	77.8	79.0	70.9	76.9	72.2
Utahwax, refined	70.4	—	70.0	—	none

*Bareco Oil Co.

Note: "R. and B. point" in the above table refers to the temperature at which the wax becomes plastic as determined by the ring-and-ball method; "softening point" to the temperature at which the wax completely softens as determined by the ring-and-plunger method; and "liquating point" to the temperature at which a heterogeneous component, if present, liquates (in the form of tiny beads) from a solid film of wax on the thermometer bulb just before the *drop point* is reached.

Specific Gravity of Waxes

	Solid		Melt
	15°/15°	25°/15°	100°/15°
Bamboo leaf wax	0.9640	0.9610	0.8190 (98°)
Bayberry	1.0262	1.0198	0.8760 (98°)
Beeswax, yellow (commercial)	0.9590–0.9640	0.9510–0.9600	0.8150–0.8290 (98°)
Beeswax, yellow, U.S.P.	0.9677	0.9580	0.8460 (98°)
Beeswax, white	0.9664	0.9547	0.8475
Candelilla wax	0.9820–0.9970	0.9807–0.9920	0.8550
Cane wax, East Indian	0.9780–0.9840	0.9720–0.9780	0.8360
Cane wax, Louisiana	0.9969	0.9919	0.8370
Cape berry wax	0.9950	0.9880	0.8740
Carnauba wax	0.9950–1.002	0.9990	0.8422 (98°)
Ceresin, imported	0.9180–0.9370	0.9100–0.9300	0.7770 (98°)
Chinese insect wax	0.9300–0.9700	0.9260–0.9660	0.8100 (99°)
Cotton wax	0.9650	——	——
Cranberry wax	0.9750	0.9700	——
Esparto wax	0.9940	0.9900	0.8370 (98°)
Fiber wax	0.9680–0.9880	0.9640–0.9480	——
Flax wax	0.9630–0.9850	——	0.8300 (98°)
Fybrene HX wax, white m. 128/133°	0.8860	0.8780	0.7820
Ghedda wax (Batavia)	0.9603	0.9504	——
Hemp wax	0.9770	——	——
I. G. Wax OP	1.0500 (?)	1.0400	0.8630 (118°)
I. G. Wax Z	0.9420	0.9360	0.7790 (112°)
Japan wax	0.9935–0.9944	0.9780	0.8730
Jasmine flower wax	0.9500–0.9710	——	0.8260
Jojoba wax	liquid at 15°	——	0.8640 (25°)
Lanolin	0.9040–0.9190	——	——
Myrtle wax	0.9950	0.9755	0.8763–0.8780 (99°)
Ouricuri wax, crude (m. 84.3°)	1.0685	1.0661	0.8990
Ouricuri wax, refined (m. 83.3°)	1.0561	1.0535	0.8650
Opalwax 10 (m. 80.0°)	0.9927	0.9893	0.8960
Palm wax	0.9950	0.9890	0.8590 (98°)
	1.0449	1.0425	
Paraffin:			
m. 121° F	0.8957	0.8780	0.7600
m. 126° F	0.9076	0.9060	
m. 131° F	0.9105	0.9020	0.7590
m. 128–130° F (commercial)	0.8783	0.8683	
m. 136° F	0.9143	0.9070	
m. 141° F	0.9147	0.9080	
m. 138–140° F (commercial)	0.9020	0.8930	0.7580
Microcrystalline waxes:			
Be-Square White, m. 160/165° F	0.9312	0.9245	0.7897 (98°)
Petrosene A, m. 167° F	0.9340	0.9255	0.7903 (100°)
Pale yellow 180, Oklahoma	0.9405	0.9375	0.7880
Ozocerite, crude	0.9520		
Ozocerite, refined (m. 75°)	0.9070	0.9033	0.7960
Raffia wax	0.9500		0.8320–0.8360
Scale wax, crude	0.8730	0.8620	0.7610 (98°)
Scale wax, refined	——	0.8210 (38°)	0.7830 (98°)
Shellac wax	0.9720 (20°)		0.8250 (98°)
Spermaceti (m. 47°)	0.9440	0.9360	0.8160 (98°)
Stearic acid U.S.P.	0.9575	0.9520	0.8325
Stearin	0.9710		
Utahwax	0.9339	0.9290	
Wool wax	0.9375		0.8850 (60°)

Coefficient of Density Change Per 1 Degree Centigrade

Kind of Wax	Temperature Range (°C)	Density Change	Density Coefficient
White microcrystalline	24–35	0.9173–0.9057	0.00102
Be-Square White	35–40	0.9057–0.9015	0.00084
m. 73.3°	83–93 (melt)	0.7990–0.7940	0.00050
	83–100 (melt)	0.7990–0.7910	0.00047
	20–30 (computed)	0.9210–0.9115	0.00095
Amber microcrystalline	20–30	0.9265–0.9201	0.00064
Petrosene A	25–45	0.9250–0.9040	0.00105
m. 75.0°	84–100 (melt)	0.7990–0.7903	0.00054
Pale yellow microcrystalline,	25–44	0.9375–0.9314	0.00032
Oklahoma	92–100 (melt)	0.7930–0.7880	0.00063
m. 86.0°	20–30 (computed)	0.9388–0.9360	0.00028
Candelilla wax, raw	27.8–44.4	0.9911–0.9823	0.00053
m. 71.0°	77–100 (melt)	0.8670–0.8550	0.00052
	20–30 (computed)	0.9940–0.9900	0.00040
Same wax, remelted	26.1–39.7	0.9803–0.9752	0.00039
	39.7–47.2	0.9752–0.9803	0.00039
	20–30 (computed)	0.9840–0.9800	0.00040
Carnauba wax, raw	25–38	1.0010–0.9980	0.00023
m. 84.2°	38–44	0.9980–0.9970	0.00017
	90–100 (melt)	0.8484–0.8415	0.00069
	20–30 (computed)	1.0020–0.9990	0.00031
Same wax, remelted	24.4–38.0	0.9990–0.9950	0.00029
	38.0–44.0	0.9950–0.9930	0.00033
	20–30 (computed)	0.9830–0.9795	0.00035
Ouricuri wax, crude	22–27	1.0668–1.0655	0.00026
m. 84.3°	27–35	1.0655–1.0626	0.00035
	27–37	1.0655–1.0616	0.00039
	95–100 (melt)	0.9010–0.8990	0.00040
Ouricuri wax, refined	24–30	1.0539–1.0516	0.00038
m. 79.0°	90–100 (melt)	0.8700–0.8650	0.00050
I. G. Wax Z	25–35	0.9360–0.9300	0.00060
m. 102°	112–122 (melt)	0.7790–0.7740	0.00050
I. G. wax OP	25–35	1.0400–1.0298	0.00102
m. 107°	118–127 (melt)	0.8630–0.8570	0.00067
Opalwax	24–35	0.9896–0.9857	0.00035
m. 80°	90–100 (melt)	0.9030–0.8960	0.00070
Bayberry wax (a)*	10.0–23.0	1.0293–1.0211	0.00063
(b)	10.0–23.0	1.0028–0.9916	0.00086
Beeswax, white	10.0–15.0	0.9698–0.9664	0.00068
m. 65.0°	15.0–25.0	0.9664–0.9547	0.00117
	71.0–96.0 (melt)	0.8671–0.8505	0.00066
Beeswax, yellow	15.0–25.0	0.9677–0.9580	0.00102
m. 64.0°	20.0–30.0 (computed)	0.9625–0.9510	0.00117
	74.0–96.0	0.8650–0.8490	0.00072
Esparto wax	12.0–15.0	0.9891–0.9880	0.00037
	15.0–25.0	0.9940–0.9900	0.00060
Ghedda wax (Batavia)	10.0–15.0	0.9649–0.9603	0.00092
	15.0–23.0	0.9603–0.9524	0.00099
Japan wax	10.0–15.0	0.9976–0.9944	0.00065
	15.0–25.0	0.9935–0.9780	0.00155
Ozocerite wax, JAA	24.0–35.0	0.9010–0.8921	0.00081
m. 75.0°	85.0–98.0 (melt)	0.8070–0.7960	0.00085
Paraffin, m. 118/120° F	10.0–15.6	0.9020–0.8950	0.00125
	15.6–25.0	0.8950–0.8780	0.00181
	57.0–100.0 (melt)	0.7800–0.7600	0.00061
Paraffin, m. 124/126° F	15.0–26.6	0.9090–0.8970	0.00106
	20.0–26.6	0.9046–0.8970	0.00115
Paraffin, m. 128/130° F	15.0–25.0	0.9086–0.8996	0.00090
	60.0–100.0 (melt)	0.7800–0.7590	0.00053

Coefficient of Density Change Per 1 Degree Centigrade (*Continued*)

	Temperature Range (°C)	Density Change	Density Coefficient
Paraffin, m. 134/136° F	10.0–15.6	0.9170–0.9140	0.00053
	15.6–25.0	0.9140–0.9070	0.00074
	20.0–30.0 (computed)	0.9110–0.9030	0.00080
Paraffin, m. 138/140° F	15.6–21.1	0.9140–0.9100	0.00073
	21.1–25.0	0.9100–0.9060	0.00100
	20.0–30.0 (computed)	0.9108–0.9010	0.00098
	70.0–100.0 (melt)	0.7780–0.7630	0.00050
Spermaceti, m. 47.0°	24.5–35.0	0.9371–0.9269	0.00091
	20.0–30.0 (computed)	0.9400–0.9315	0.00085
	56.0–100.0 (melt)	0.8370–0.8120	0.00057

*Specimens (a) and (b) taken from same lot of pure material; (b) assumed to be more porous than (a).

Coefficient of Cubical Expansion of Waxes

	Solid/25°	Melt/100°
Beeswax, yellow	0.00123	0.000918
Beeswax, white	0.00126	0.000873
Candelilla wax	0.000404	0.000608
Carnauba wax	0.000310	0.000820
Ceresin, artificial (m. 166° F)	———	0.000585
I. G. wax OP	0.000990	0.000782 (melt/110°)
I. G. wax Z	0.000645	0.000646 (melt/110°)
Microcrystalline waxes:		
160–165 Be-Square White	0.001042	0.000594
Petrosene A, m. 167° F	0.000696	0.000683
180 Pale yellow, Oklahoma	0.000299	0.000800
Opalwax	0.000355	0.000781
Ouricuri wax, crude	0.000244	0.000604
Ouricuri wax, refined	0.000361	0.000668
Ozocerite, JAA (m. 161° F)	0.000908	0.001068
Paraffins:		
m. 121° F (47.2° C)	0.002061	
m. 126° F (52.2° C)	0.001282	
m. 131° F (55.0° C)	0.000943	
m. 136° F (57.5° C)	0.000886	
m. 141° F (60.5° C)	0.000818	
m. 128–130° F (S.O.N.J.)	0.001000	0.000685
m. 138–140° F (S.O.N.J.)	0.000993	0.000655
Spermaceti	0.000972	0.000702

Note: The coefficient of expansion is calculated for each wax from the formula $\beta = \frac{d_1 - d_2}{d_2 t}$ derived from the formula $\beta = \frac{v_2 - v_1}{v_1 t}$, where t is the difference in temperature at which the density determinations are taken, and v_2 and v_1 represent the volumes of 1 gram of wax at temperatures t_2 and t_1. The coefficient for the waxes in liquid condition is taken between 10° above melting point and 100°.

Volume Decrease of Waxes During Solidification and Crystallization

Computed by Graef's Formula : $C = 100\text{–}100 \dfrac{\text{density liquid}}{\text{density solid}}$

For computation the density of the melt is taken at 10 degrees above melting point; the density of solid is taken at 25°.

	(%)
Waxes from Insects:	
Apis—	
Beeswax	9.70
Ghedda wax	9.45
Coccid—	
Chinese insect wax	15.18
Shellac wax	14.55
Waxes from Animals:	
Land—Wool wax	8.00
Marine—Spermaceti	10.58
Waxes from Plants:	
Palm tree group—	
Carnauba wax	15.35
Curicuri wax	17.47
Bamboo wax	14.15
Palm wax	13.40
Shrubs and canes—	
Candelilla wax	11.80
Sugar cane wax	14.85
Fibers and grasses—	
Esparto wax	14.88
Flax wax	13.76
Raffia wax	11.70
Waxes from Berries—	
Cranberry wax	——
Bayberry wax	9.10
Japan wax	9.80
Hydrocarbons:	
Paraffin, m. 128–130° F*	12.46
Paraffin, m. 138–140° F*	14.46
Microcrystalline, m. 160° F	12.87
Slack wax	11.00
Synthetic wax:	
Opal wax	6.00
Stearic Acid:	
Commercial stearic acid	12.16

**Note*: Contraction of the paraffins varies between 11 and 15 per cent.

Comparison Between Melting Points of Petroleum Ceresin Waxes by ASTM (D 127–30) and Fisher-Johns Methods

Sample	ASTM (°F)	Fisher-Johns (°F)
Gargoyle Petrosene A	171	165
Light Yellow Sunwax (Sun Oil Co.)	180	176
Amor A Wax (Petrolite Corp. Ltd.)	192	186
Be-Square White (Bareco Oil Co.)	172	169
Be-Square Amber 190/195	192	189
Amber Micro (Allied Asphalt & Mineral Corp.)	183	176

Solubility of Waxes in 95 Per Cent Alcohol U.S.P.
(expressed in grams per 25 ml. of solvent at 25°)

Ouricuri wax	0.163
Beeswax	0.327
Ozocerite	0.175
Shellac wax	0.0675
Japan wax	1.425
Bayberry wax	0.907
Esparto wax	0.244
Spermaceti	0.601
Sugar cane wax	1.465

Solubility of Carnauba Wax in Various Solvents
(expressed in grams per 25 ml of solvent at 25°)

Ethyl ether	0.421
Methanol	0.179
Ethanol 95%, U.S.P.	0.141
Benzene	0.518
Chloroform	1.690
Acetone	0.323
Xylol	0.610
Turpentine, gum spirits	0.144
Naphtha ("Varnoline")	0.2188
Ethyl acetate	0.374

Solubility of Waxes in Ethylene Dichloride
(expressed in grams per 100 ml of solvent at advanced temperatures)

	At 37°
Ouricuri	0.348
Beeswax	3.420
Ozocerite	2.620
Shellac wax	1.190
Japan wax	54.60
Bayberry wax	30.24
Esparto wax	1.480
Spermaceti	50.30
Sugar cane wax	1.610

Solubility of Beeswax in Various Solvents
(expressed in grams per 100 ml total solvents plus wax)

	At 25°	At 35°	At 45°
Ethanol 95% U.S.P.	0.340	0.775	1.220
Benzene	16.900	33.300	43.900
Ethylene dichloride	2.300	5.700	19.000

Saponification Values for Natural Waxes

Fatty waxes:

Insects—Coccid	Scale insect species 210–216
Barks	Ocatilla 182–188
Fruits and berries	Cochin China wax 232–238; Japan wax 207–238; Myrtle wax 205–216

Medium high saponifiable:

Shrubs and canes	Madagascar waxes 140–160
Fibers and grasses	Cotton 159–178
Fruits and berries	Cranberry 118–157

Medium low Saponifiable:

Insects—Coccid	Ceroplastes saponification 98–153; Chinese insect wax 78–93; Shellac wax 120–126
Insects—Apis	Beeswax 88–106; Ghedda wax 86–130; Trigona saponification 80–146
Animals—Land	Wool wax 82–140; Mutton bird oil 123–144; Silk cocoon wax 105–115
Animals—Marine	Sperm oil 123–133; Bottle-nose oil 123–144; Spermaceti 120–135
Palm tree group	Palm wax (pure) 101–106; Pisang wax 106–112
Shrubs and canes	Snow brush wax 90–96; Sugar cane wax (crude) 98–168
Fibers and grasses	Hemp 101–140
Roots and rhizomes	Dandelion root wax 112–118
Seed	Soybean wax 100–106; Jojoba wax 90–96

Low saponifiable:

Palm tree group	Carnauba wax 78–84; Ouricuri wax 62–109; Bamboo wax 41–46; Raffia wax 50–54
Shrubs and canes	Candelilla wax 47–65; Sugar cane wax (refined) 57–98
Fibers and grasses	Flax wax 70–84; Esparto wax 67–73; Fiber wax 61–76
Roots and rhizomes	
Barks	Oleander bark wax 50–56
Flowers	Jasmine wax 65–69; Rose wax 30–35

Two-Way Temperature Conversion Table

(°C)		(°F)	(°C)		(°F)	(°C)		(°F)
-40.0	**-40**	-40	2.78	**37**	98.6	21.7	**71**	159.8
-34.4	**-30**	-22	3.33	**38**	100.4	22.2	**72**	161.6
-28.9	**-20**	- 4				22.8	**73**	163.4
-23.3	**-10**	14				23.3	**74**	165.2
-17.8	**0**	32				23.9	**75**	167.0
-17.2	**1**	33.8				24.4	**76**	168.8
-16.7	**2**	35.6				25.0	**77**	170.6
-16.1	**3**	37.4				25.6	**78**	172.4
-15.6	**4**	39.2				26.1	**79**	174.2
-15.0	**5**	41.0	3.89	**39**	102.2	26.7	**80**	176.0
-14.4	**6**	42.8	4.44	**40**	104.0	27.2	**81**	177.8
-13.9	**7**	44.6	5.00	**41**	105.8	27.8	**82**	179.6
-13.3	**8**	46.4	5.56	**42**	107.6	28.3	**83**	181.4
-12.8	**9**	48.2	6.11	**43**	109.4	28.9	**84**	183.2
-12.2	**10**	50.0	6.67	**44**	111.2	29.4	**85**	185.0
-11.7	**11**	51.8	7.22	**45**	113.0	30.0	**86**	186.8
-11.1	**12**	53.6	7.78	**46**	114.8	30.6	**87**	188.6
-10.6	**13**	55.4	8.33	**47**	116.6	31.1	**88**	190.4
-10.0	**14**	57.2	8.89	**48**	118.4	31.7	**89**	192.2
- 9.44	**15**	59.0	9.44	**49**	120.2	32.2	**90**	194.0
- 8.89	**16**	60.8	10.0	**50**	122.0	32.8	**91**	195.8
- 8.33	**17**	62.6	10.6	**51**	123.8	33.3	**92**	197.6
- 7.78	**18**	64.4	11.1	**52**	125.6	33.9	**93**	199.4
- 7.22	**19**	66.2	11.7	**53**	127.4	34.4	**94**	201.2
- 6.67	**20**	68.0	12.2	**54**	129.2	35.0	**95**	203.0
- 6.11	**21**	69.8	12.8	**55**	131.0	35.6	**96**	204.8
- 5.56	**22**	71.6	13.3	**56**	132.8	36.1	**97**	206.6
- 5.00	**23**	73.4	13.9	**57**	134.6	36.7	**98**	208.4
- 4.44	**24**	75.2	14.4	**58**	136.4	37.2	**99**	210.2
- 3.89	**25**	77.0	15.0	**59**	138.2	37.8	**100**	212.0
- 3.33	**26**	78.8	15.6	**60**	140.0	43	**110**	230
- 2.78	**27**	80.6	16.1	**61**	141.8	49	**120**	248
- 2.22	**28**	82.4	16.7	**62**	143.6	54	**130**	266
- 1.67	**29**	84.2	17.2	**63**	145.4	60	**140**	284
- 1.11	**30**	86.0	17.8	**64**	147.2	66	**150**	302
- 0.56	**31**	87.8	18.3	**65**	149.0	71	**160**	320
0	**32**	89.6	18.9	**66**	150.8	77	**170**	338
0.56	**33**	91.4	19.4	**67**	152.6	82	**180**	356
1.11	**34**	93.2	20.0	**58**	154.4	88	**190**	374
1.67	**35**	95.0	20.6	**69**	156.2	93	**200**	392
2.22	**36**	96.8	21.1	**70**	158.0	99	**210**	410
						100	**212**	413

Example 1. 42° Fahrenheit to be converted to Centigrade: Find 42 in the center column (*bold face type*) and read 5.56° C to the left.

Example 2. 42° Centigrade to be converted to Fahrenheit: Find 42 in the center column (*bold face type*) and read 107.6° F to the right.

Author Index

[*Page in bold face indicates that author's name appears in the reference list on that page.*]

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