# THE ANIMAL AND VEGETABLE WAXES IN 1938

### By L. WILSON GREENE

ABERDEEN, MARYLAND

MPORTS of animal and vegetable waxes into the United States during 1938 amounted to about 20,000,000 pounds, valued at \$5,000,000 Jp 1027

at \$5,000,000. In 1937 the figures were 26,500,-000 pounds and \$7,500,-000, respectively. According to statistics compiled by the Chemical Division of the U. S. Department of Commerce, imports during the past 10 years have increased over 60%.

The most significant American development relating to wax technology during the year was the research conducted at Marquette University on the melting points of binary and trinary mixtures of several commercial waxes and wax-like products. The data obtained are of value in analyzing wax mixtures and in choosing the proper

mixture to give a desired melting point. Investigations conducted in the laboratories of the American Gum Importers Association yielded useful information on the properties of mixtures containing waxes and natural resins.

The composition and hydrogenation of sperm oil continued to receive attention in Russia and in Japan. Further studies were reported from the latter country on the composition of wool fat; two new alcohols, lanooctadecyl alcohol and lanyl alcohol, being discovered in the unsaponifiable portion of this wax. A method for isolating pure cholesterol from wool fat was also developed in Japan.

#### ANIMAL WAXES Beeswax

When Formosan bees collect nectar from citrus trees, the wax produced has an entirely different composition than ordinary beeswax. C. Hata (J. Chem. Soc. Japan 58, 1188-92) found that such wax contained 80% unsaponifiable matter consisting of 28% alcohols and 72% hydrocarbons. Hentriacontane and ceryl alcohol formed the

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principal constituents of the unsaponifiable portion, while small amounts of melissyl alcohol, nonacosane, heptacosane and pentacosane were isolated. The fat acids consisted mainly of palmitic acid with lesser amounts of oleic, cerotic and melissic acids.

A sample of beeswax from Gambia was examined at the Imperial Institute (*Bull. Imp. Inst. 36*, 153-7) and was found to have characteristics agreeing closely with those reported in 1935 (*Chem. Abs. 30*, 626).

The production of beeswax in Anglo-Egyptian Sudan was described by L. W. Greene (Am. Bee J. 78, 118-9). Crude production methods employed by the natives yield an inferior grade of wax.

An interesting fact about the Japanese wild bee was discovered by S. Ueno and S. Komori (J. Soc. Chem. Ind., Japan 40, Suppl. binding 432-4). They observed that the comb oil of Vespa mandarina consists mostly of palmitic, oleic and

linolic acids, and the unsaponifiable matter contains oleyl alcohol and hydrocarbons. Ordinary beeswax, on the other hand, contains higher saturated fatty

> acids. F. Neuber (Seifensieder-Ztg. 64, 652) developed a method for recovering wax from old honeycomb and lowgrade press residues by agitating them with hot solutions of such wetting agents as Nekals, Igepons, etc. The purified wax arises to the surface, leaving the impurities in the aqueous phase.

A process for bleaching beeswax was patented by D. J. Campbell and L. P. London (U. S. 2,108,282; see also U. S. 2,113,433). A solution of hydrogen peroxide is added to the molten wax in the presence of zinc oxide, the

latter acting as a bleaching promoter.

J. T. MacMillan (Am. Bee J. 78, 457) described numerous household uses for the wax and H. Schwarz (Seifensieder-Ztg. 65, 382) summarized the characteristics of pure beeswax and discussed the effects of adulterants and bleaching on these properties. L. W. Greene (Am. Bee J. 78, 462) reviewed the progress in beeswax technology in 1937.

#### Wool Wax (Wool Fat, Wool Grease, Lanolin)

The so-called "frosted wool process" for separating the grease from raw wool was described by H. C. Turner (*Refrig. Eng. 34*, 364-6). The wool is cooled to -30° to -50° F. and the grease is thus congealed to a brittle condition so that dusting shakes it off, together with other impurities. The treatment removes about 33% of the grease and up to 90% of dirt and other extraneous matter. Patents relating to the method were granted to R. J. Wig (U. S. 2,116,-294) and the California Process Co. (*Brit.* 485,543).

According to H. W. Fawcett (*Textile*  $M\bar{f}r$ . 63, 487) the cost of wool scouring can be reduced by using cleansed washing liquors over again. This is made practical by the development of high-speed centrifugals. W. E. Fitzpatrick (Australian 102,271; Brit. 482,-748; Fr. 827,376) described a bath for removing fat from raw wool. He employed pyridine (or its derivatives or homologs) together with ammonia and soap or soda ash in the scouring bath. Fatdissolving agents used in refining wool were reviewed by W. Pflumm (Spinner u. Weber 56, No. 9, 36-41). Hansawerke Lürmann, Schütte & Co. (Ger. 656,111) was granted a patent on a method for recovering crude wool fat from wool-scouring water. A sulfonated fat or an acid sulfate of a higher alcohol, more stable than soap, is used in the bath and the wash water is slightly acidified with sulfuric acid and allowed to stand. The mixture is then made slightly alkaline with calcium hydroxide, forming a precipitate which carries down the wool fat with it. W. Weiler (Deut. Färber-Ztg. 74, 27) stated that aluminum is unsatisfactory for use in wool-scouring equipment because it is attacked by the suint (sweat) from the wool. The effect of waste waters from wool scouring on sewage treatment was discussed by A. D. Weston (Sewage Works J. 9, 970-85).

T. Kuwata (J. Am. Chem. Soc. 60, 559-60), continuing his work on the composition of wool wax, reported the properties of lanopalmic acid isolated from the scouring liquor from merino wool. The acid has the formula  $C_{16}H_{32}$ -O<sub>3</sub>, melts at 86-7° and has  $[\alpha]D-1°$ . Its methyl ester boils at 230-1°/5mm., melts at 45-6° and has  $[\propto]D-1.5^{\circ}$ . The optical rotation was determined in ethyl alcohol solution. Magnesium lanopalmate is insoluble in boiling alcohol and melts above 280°. When methyl lanopalmate is oxidized by chromic acid in acetic acid solution, methyl lanopalmionate (m. p. 47-47.5°) is formed. This is identical with with 30% hydrogen peroxide gives pentadecylic acid. Oxidation of lanopalmic acid with lead peroxide yields pentadecylic aldehyde. The acid, which comprises about 6% of

the fat acids of wool wax, is a stereoisomer of  $\infty$ -hydroxypalmitic acid.

Two new alcohols were discovered in wool wax by T. Kuwata and M. Katuno (J. Soc. Chem. Ind., Japan 41, Suppl. binding 227-8). The alcohols were isolated from the unsaponifiable matter by crystallization fractional from methyl alcohol, followed by further fractionation from acetone at -10°. The liquid portion remaining after this treatment was acetylated and fractionally distilled in vacuum. Lano-octadecyl alcohol, melting at 42.3°, and lanyl alcohol, melting at 78.5°, were isolated from the distillation products. The melting point of the latter alcohol rose to 79.5-80° after it had been dried for one month in a desiccator. Lanyl alcohol has the formula  $C_{21}H_{40}(OH)_2$  and does not absorb bromine at room temperature.

These same workers (Ibid. 228-9) devised a method for isolating cholesterol from wool wax. They plotted curves for the solubility of cholesterol and isocholesterol in benzene, petroleum ether, acetone, dioxane and ethyl alcohol at various temperatures but none of these solvents was found to be useful for separating cholesterol. In methyl alcohol, however, isocholesterol has a low solubility even at high temperatures and this fact was used as the basis for the separation method. Hot methyl alcohol was employed to extract the unsaponifiable portion of wool wax and the crude cholesterol was precipitated by cooling to room temperature. Pure crystallized cholesterol, melting at 145-6°, was obtained by recrystallizing the precipitate from either ethyl alcohol or ethyl acetate.

A. Heiduschka and E. Nier (J.prakt. Chem. 149, 98-106) found that saponification of wool fat yielded 62.7% fat acids, 32.8% unsaponifiable matter and 1.1% material insoluble in ether. By fractionation of the fat acids, cerotic acid (m. p. 78°) and lanoceric acid (m. p. 102.5°) were identified. The following esters were prepared: propyl cerotate (m. p. 65. 5°). iso-propyl cerotate (m. p. 75°), *iso*-butyl cerotate (m. p. 65.5°), amyl cerotate (m. p. 63°) and ethyl lanocerate (m. p. 78°). The unsaponifiable portion was reported to contain cervl alcohol, isocholesterol and cholesterol. The presence of carnaubyl alcohol, stated by Darmstaedter and Lifschütz in 1896 to be a constituent of wool

fat, could not be confirmed. At least two other compounds which could not be isolated in pure form are believed to be present.

Although the literature continues to report that isocholesterol is a constituent of wool fat, P. Mohs (*Fette u. Seifen 45*, 152-4), after making a critical review of published work, states that cholesterol and dihydrocholesterol are the only sterols whose presence has been definitely established. There is some evidence that ergosterol may also be present.

The preparation of cholesterol esters was described in a patent granted to E. A. Mauersberger (Ger. 657,705). Wool fat alcohols, obtained from wool fat by saponification and distillation or extraction, are fractionally distilled in a high vacuum. The cholesterol is contained in the fraction boiling above 230°. The fraction is esterified with commercial boric acid. the boric ester of oleyl alcohol is added, and 95% sulfuric acid is stirred in. The mixture is cooled in order to hold the temperature at 35°. The product, cholesterol sulfuric ester, is a yellow hygroscopic powder.

A process for splitting wool fat into fat acids and alcohols was described by Metallgesellschaft A.-G. (Ger. 656,556). The material is subjected to a long steam distillation at atmospheric pressure, the temperature being about 400°. Then the distillate is saponified with sodium hydroxide and the resulting product is distilled at high vacuum and low temperature, thereby removing the unsaponifiable part (alcohols). The soap remaining in the still is treated with sulfuric acid to liberate the fat acids.

The I. G. Farbenindustrie A.-G. obtained a patent (Brit. 483,315) covering the manufacture of a colloidal product from wool fat. The material itself, or a purified fraction derived from it, is mixed with an alkali metal and heated at an elevated temperature. An organic solvent indifferent to the metal may be added. Any undissolved metal is removed by filtration and the solvent (if used) is evaporated, leaving a product having a soft, wax-like consistency. Upon trituration with a small amount of water, the product forms a creamy emulsion which yields a weakly alkaline emulsion on further dilution. Another colloid product was described by H. Cohn and C. Siebert (U. S. 2, 100, 067).

#### oil & soap

According to L. Haskó (Vegyi Ipar 37, No. 7, 1), the moisture in neutral wool fat can be determined by simply drying the sample, but if a considerable amount of acid is present distillation with xylene is necessary. The following procedures are recommended for the analysis of wool fat: ash by the usual methods, iodine number by the methods of Wijs or Hanus, saponification value by Jungkunz's method, and unsaponifiable matter by the method of Lifschütz. S. D. Roussouw (Onderstepoort J. Vet. Sci. Animal Ind. 10, 229-33) developed a method for the accurate determination of wool fat in raw wool. A 50-gm. sample of greasy wool from the right shoulder is stored at 21.5° and 70% relative humidity until it reaches constant weight. The sample is then placed in a fine-textured Whatman extraction thimble and dried for at least 12 hrs. over sulfuric acid at 70° in a vacuum of 25 mm. The thimble is weighed quickly and is then placed in a Soxhlet extractor having a calcium chloride tube attached to the condenser. The sample is extracted 10 times with petroleum ether having a boiling point of approximately 45°. The solvent is then evaporated at 50° and the extraction flask is dried to constant weight in a vacuum desiccator at 75° and 25 mm.

B. A. Ryberg (Am. Dyestuff Reptr. 27, Proc. Am. Assoc. Textile Chem. Colorists P8-13) described a method for determining the grease content of raw wool, using ethyl alcohol as the extracting solvent.

Numerous industrial uses for lanolin were described briefly (*Industrial Chemist 14*, 416-7) and L. W. Greene (*Textile Colorist* 60, 153-6) reviewed the progress in wool fat technology in 1937.

### Sperm Oil and Spermaceti

Studies on the composition of sperm oil were continued in Japan (see wax review for 1937 in this journal). M. Tsujimoto and H. Koyanagi (J. Soc. Chem. Ind., Japan 40, Suppl. binding 315-17) distilled sperm blubber oil under a vacuum of 2 mm., obtaining 60.25% of distillate. While the unsaponifiable matter in the original oil was 34.64%, that in the distillate amounted to 47.47%. Most of the glycerides remained in the distillation residue. Attempts to separate the esters by fractionating the distillate were unsuccessful but there was evidence to support the belief that it consisted mostly of cetyl or oleyl esters of oleic acid, together with an appreciable quantity of esters of  $C_{16}$  acids mainly zoömaric. A small amount of cetyl palmitate was identified.

The same workers (*Ibid.* 41, Suppl. binding 41-3) distilled bottlenose oil (Arctic sperm oil) under a 2-mm. vacuum and identified oleyl oleate and cetyl oleate in the fractions. They also found  $C_{16}$ and  $C_{20}$  acids in the lower and higher boiling fractions, respectively.

Y. Toyama (J. Chem. Soc. Japan 59, 810-14) isolated eicosanol and eicosenol  $(C_{20}H_{40}O_2)$  from the 'unsaponifiable portion of sperm blubber oil. The latter alcohol, when converted into its acetate and oxidized with potassium permanganate, gave indication that it is a monoethylenic alcohol corresponding to  $\Delta^{9, 10}$ -eicosenoic acid.

In the refining of sperm oil and other materials containing natural wax-like esters, W. Holwech (*Brit.* 479,758) proposed a vacuum distillation method in which the temperature is sufficiently high to evaporate the wax esters in an unsplit condition, leaving the facts in the residue.

A. A. Bag and T. P. Egupov Nauch-Issledovatel. (Vsesoyuz. Inst. Zhirov, Hydrogenation of Oils 1937, 146-58 (in English 158-9)) hydrogenated sperm oil by the drip method with a stationary catalyst. The product melted at 50-51° and had an iodine number of 10. When temperatures above 200° were employed, volatile substances were distilled and these were thought to be products resulting from the decomposition of the oil. Hydrogenation with a powdered catalyst proceeded with difficulty and two or three times the normal amount of catalyst was required. When both hydrogenated and untreated oil were hydrolyzed with the Petrov contact mixture, only the glycerides were decomposed and the waxes remained unchanged. The best method for the laboratory or factory separation of waxes and fat acids in the saponification products of hydrogenated sperm oil involves treatment with alcohol and pressing. It was also found that 7 to 8% of spermaceti can be separated from the body oil by preliminary freezing fol-lowed by pressing. The investigation indicated that the hydrogenated oil can be substituted for

stearic acid in candle manufacture and that the fats obtained from the oil may be used for making laundry and toilet soaps.

Another study on the hydrogenation of this wax was conducted in Russia by T. A. Belova (Masloboino Zhirovoe Delo 13, No. 6). Standard quality spermaceti was obtained by treating the hydrogenated product with hot 96% alcohol. The triglycerides were not dissolved. Cetyl alcohol was produced by Lang's method (Chem. Abs. 28, 259), modified by using alcoholic solutions with a large excess of potassium hydroxide and precipitating the fat acids with barium chloride instead of calcium chloride. This change resulted in a colorless product. Myristyl, octadecyl and other higher alcohols were made from hydrogenated sperm oil by saponifying with a 15% alcoholic solution of potassium hydroxide, using a 4% excess. The mixture was heated for 1 hr. and then diluted with 90% alcohol and precipitated with hot 25% barium chloride solution. The solvent was evaporated and the higher alcohols were obtained by three triturations with ethyl alcohol. Decolorizing carbon was employed to obtain a colorless product. It was suggested that the product might be used in the preparation of cosmetics.

H. Gault and E. Beloff (Bull. soc. chim. (5) 5, 295-304) isolated cetyl palmitate from spermaceti and produced gasoline fractions by cracking the ester in the presence of aluminum chloride. The spermaceti obtained during the first German whaling expedition in 1936-7 was analyzed by H. Leue (Fette u. Seifen 45, 52-8).

#### Other Animal Waxes

The occurrence and distribution of wax in raw silk was studied by W. Bergmann (Textile Research 8, 195-9, 221-5; Ann. Entomol. Soc. Am. 31, 315-21). He found that the ether-soluble fraction of white Chinese silk consists of a mixture of normal primary alcohols and acids of the order  $C_{26}$ - $C_{32}$ , paraffins of the order C25-C31, and liquid fat acids. This ether-soluble fraction, consisting primarily of silk wax, is not evenly distributed in the cocoon. The wax content decreases from the external to the internal layers in yellow Italian and white Chinese cocoons. It is also reported that the cuticulin of the silkworm (Bombyx mori) is a

A. Karim (Indian Lac Research Inst. 1937, 21pp.) determined the electric properties of shellac and concluded that the presence of wax does not appear to affect these properties but it does facilitate molding. The breakdown voltage of shellac wax is practically the same as for shellac itself but the dielectric strength of the former is considerably less. The dielectric strength of shellac wax varies from 356 to 418 volts per mil.

The composition of two marine animal oils was investigated by M. Tsujimoto and H. Koyanagi (J. Soc. Chem. Ind., Japan 40, Suppl. binding 403-5) by vacuum distillation and identification of the fractions. Inguandaramé oil was reported to contain cetyl and oleyl oleates as well as about 5% of glycerides. Karasumi oil was found to comprise 11% of glycerides and the cetyl and octadecenyl esters of oleic acid. Wax esters of acids more unsaturated than oleic were isolated together with a small amount of what was thought to be cetyl clupanodonate.

#### VEGETABLE WAXES Carnauba Wax

According to a patent issued to the Deutsche Hydrierwerke A.-G. and W. Schrauth (*Ger.* 658,749), carnauba wax may be bleached by heating it at a raised temperature in the presence of an alkali metal and an alcohol. In an example the wax is first dissolved in butyl alcohol and metallic sodium is added.

H. Limburg (*Chem. Weekblad* 34, 716-19) used a carnauba wax surface in a study of wetting phenomena. He determined the variations with time in the angle formed by a drop of a 0.1% solution of a wetting agent on such a surface.

#### Cane Wax

Further work on the components of cane wax by T. Mitsui (J. Agr. Chem. Soc. Japan 14, 342-8) was concerned with the oxidation of cane-sitosterol. Hot acetone was used to extract the unsaponifiable portion of the wax and the solution was allowed to cool. A precipitate formed and was filtered off. Evaporation of the filtrate yielded light yellow crystalline plates which were first acetylated and then brominated. Stigmasterol acetate bromide and sitosterolin acetate dibromide were formed. Oxidation of the latter by chromic acid yielded *trans*-dehydandrosterone, ketones and complex acids. A constitutional formula for cane-sitosterolin was proposed.

K. L. Khanna (Dept. Agr., Bihar and Orissa, Bull. No. 6 of 1934, 47 pp.) stated that the amount of wax on the stalk has an effect on the germination of sugar cane pieces. The tendency to germinate decreased with increase in the amount of wax.

A bacterial method for preventing the rotting of bagasse results in a lower wax content, according to O. Kühne (Zellstoff u. Papier 17, 526-31).

#### Cotton Wax

Analyses made by I. I. Vadimovich (Mem. Inst. Chem. Tech., Acad. Sci. Ukrain. S. S. R. No. 9, 3-14 [in English 16-17]) showed that Ukrainian cotton crops contained an average of 0.9 and 1.2% of fats and waxes in 1934-5 and 1936, respectively.

A method for treating cotton with ammonium hydroxide to soften the wax and effect mercerization was proposed by W. B. Pratt (U. S. 2,126,809). The effect of solvents on the removal of wax from unbleached cotton before boiling-out was studied by L. Kollman (*Melliand Textilber*, 19, 269-71). It is stated that the value of solvents for dewaxing is overestimated and that good results can be obtained with a 1% solution of sodium hydroxide.

#### Montan Wax

A commercial process is being used in Poland for the extraction of montan wax from peat. W. Stefanowski and Z. Dominik (Przeglad Chem. 1, 73-6) reported that Polish peat contains 8 to 17% wax and that the crude product has the following characteristics: m. p. 81-3°, acid value 40-43, esterification value 25 to 29, saponification value 65 to 72, solubility in ether 35 to 70%, insoluble in benzene 1%, ash 1.1 to 0.5% and sp. gr. 1.030. The crude wax was extracted with alcohol to produce five fractions: a soft resin 6.5, a resin (m.p. 67-8°) 6.5, wax contaminated with resins 32, pure wax (m.p. 82-4°) 15 and asphalt residue 40%.

J. Reilly, D. F. Kelley, D. J. Ryan and E. Boyle (*Brit.* 486,383) produced a wax by extracting peat with a mixture of two or more wax solvents of constant boiling point. Numerous binary and trinary azeotropes were proposed as solvents.

– oil & soap

Extraction products of coal are separated into a wax fraction and an asphalt fraction by mechanical methods, according to a patent obtained by the I. G. Farbenindustrie A.-G. (Brit. 481,108). Suitable methods involve sedimentation by centrifuging. The wax fraction is purified by treatment with selective solvents and the product may be used in wax-containing compositions. The hydrogenation products of this wax fraction are suitable for use as lubricating, Diesel and illuminating oils or they may be cracked to form gasoline.

D. J. W. Kruelen and N. M. Roodenburg (*Chem. Weekblad 34*, 649-50) compared the temperaturesurface tension curves of bitumens obtained from different kinds of coal with those from low-temperature tars and montan wax.

The fused wax may be bleached by treating it in succession with a solution of hydrogen peroxide and a chromic acid solution, according to a patent granted to the I. G. Farbenindustrie A.-G. (Fr. 829,-021). A method for deresinifying and bleaching montan wax was developed in Russia by A. Davankov and O. A. Konovalova (Org. Chem. Ind. [U.S.S.R.] 4, 376-9). Instead of using inflammable solvents for refining the wax, the following procedure was devised: the crude wax was dissolved in 4 volumes of dichloroethane, the solution was cooled to room temperature (or preferably to  $0^{\circ}$ ) and the separated wax was filtered off. The residue on the filter was then washed with 10 to 20 volumes of dichloreothane and heated to remove the occluded solvent. Commercially, the process can be conducted more efficiently by concentrating the brown coal extract to the required volume and then following the method outlined above. The resulting dark product melted at 80-86° and had acid value 34 and saponification value 92. It was bleached by dissolving it in dichloroethane and treating with nitrogen tetroxide for 5 to 7 hrs., the solution being heated at 70-90°. The wax that separated on cooling the solution was heated to expel the bleaching agent and was then oxidized 3 to 4 times at 80-90° with 1.5-2% of potassium dichromate in 25% sulfuric acid solution. The product had a pale yellow color, was porous and melted at 80-90°.

The yield was between 75 and 78%.

K. B. Vaisel'berg (Khim. Tverdogo Topliva 8, 232-246) extracted montan wax from a Russian brown coal, using a solvent composed of equal parts of benzene and alcohol. The crude extract had acid value 34.7, ester value 103.5, saponification value 138.2, I no. 51.7 and ash 1.20%, and contained 32.5% tar and 67.5% wax. The hydrogenation products of the crude wax were investigated. C. R. Kent (Proc. Roy. Soc. [London] A163, 568-74) found 0.5% of a brown wax in a sub-bituminous coal from Western Australia.

#### Other Vegetable Waxes

M. Meyer (Protoplasma 29, 552-86) studied the sub-microscopic structure of the cutinized cell membrane in four plants. She examined the cuticular layers of Clivia, Yucca, Gasteria and Dasylirion and found that the layer consisted of two components, a fusible substance and a non-fusible framework. The former comprised a substance that could be extracted with fat solvents, the so-called cutin wax. This forms tangentially oriented plate-like micelles which are doubly refracting and have the structure of known paraffin micelles. It is believed that the wax molecules lie parallel to the surface. The bibliography appended to the paper contains 61 references.

F. Zetsche and E. Lüscher (*J. prakt. Chem. 150,* 68-80) reported that cork wax contains the following: arachic acid 1, cerotic acid 1,  $\alpha$ -oxyarachic acid 1.5, phellonic acid 0.5, oleic acid 1, linoleic acid 1.5, friedelin and cerin 18-19, an acid C<sub>30</sub>H<sub>48</sub>O<sub>3</sub> 2, an alcohol C<sub>24</sub>H<sub>42</sub>O<sub>2</sub> 2.1, phytosterol 0.6 and a mixture of sterols 10%.

According to R.-H. Kimm (*Sci. Papers Inst. Phys. Chem. Res.* (Tokyo) 34, 637-77 (in English), the crude fat extracted from rice embryo contains a wax which is mostly melissyl cerotate. A. Ichiba (*Ibid. 34, 132-6*) identified ceryl alcohol in the unsaponifiable portion of lettuce oil and, from the same component of wheat-germ oil, he obtained an oily alcohol ( $C_{29}H_{50}$ - $O_2$ ) and eicosanol (*Ibid. 34, 121-31*).

Melissic acid was identified in the petroleum ether extract of *Ipomea pes-caprae* by G. E. Cwalina and G. L. Jenkins (J. Am. Pharm. Assoc. 27, 585-95), and E. J. Fellows and C. S. Smith (*Ibid*.

27, 565-73) found melissyl alcohol, five fat acids and a sterol in the solvent extract of Passiflora incarnata. L. S. Malowan (Arch. Pharm. 276, 150-4) noted the presence of a wax in Cannabis sativa. A small quantity of melissyl alcohol was isolated from the leaves of Premna odorata by P. Sunico-Suaco and P. Valenzuela (Rev. filipina med. farm. 29, 207-20). Chibnall and co-workers (Biochem. J. 31, 1981-6) investigated the wax from the leaves of Santalum album. They found two new substances not previously reported to be present in waxes: palmitone and d-10-hydroxypalmitone. The unsaponifiable portion of the wax contained 75% octacosanol and 25% triacontanol.

A soft, aromatic, green-brown wax, containing higher alcohols, was extracted from Gnaphalium obtusifolium by P. J. Jannke (Pharm. Arch. 9, 17-48). A brittle concrete containing considerable wax was obtained from the flowers of Syringia vulgaris by G. Igolen (Parfums France 16, 92-3) and F. W. Friese (Samml. Vergiftungsfällen 7, Abt. C, 1-8) isolated a poisonous gray-green wax from the wood of *Bignoniaceae*. The latter worker (Pharm. Zentralhalle 79, 49-51) also found 0.50-1.50% wax in the leaves and flowers, respectively, of Carex arenaria. G. Giacomello (Gazz. chim. ital. 68. 363-76) investigated the unsaponifiable portion of violet wax and Y. Nakamura and K. Hess (Ber. 71B, 145-52) reported on the wax content of maize and oat coleoptiles.

A. Shmuk (Vsesovuz. Inst. Tabach. i Makhoroch. Prom. No. 133. 3-9 [in English 9]) stated that tobacco leaves contain 0.15% of wax. L. Robinson-Gomez and L. L. Leonico (Univ. Philippines Nat. and Applied Sci. Bull. 6, 97-101) found 1.76% of waxes and fats in air-dried banana straw and H. Wagner (Z. Untersuch. Lebensm. 76, 1-20) attempted to separate the fat acids of the wax-like portion of the coffee bean but the results were inconclusive. E. R. Schafer and C. E. Curran (U. S. Forest Products Lab. Mimeographed Report R1159, 28 pp.) discussed the possibilities of the commercial utilization of flax wax as a by-product of papermaking when using seed flax straw. K. S. Markley, C. E. Sando and S. B. Hendricks (J. Biol. Chem. 123, 641-54) found fat acids, including higher saturated acids of the series C<sub>20</sub> to C<sub>32</sub>, primary alcohols of the series C22 to C28, higher hydrocarbons and a sterol in the extractives of grape pomace from Concord grapes (Vitis labrusca). Approximately 4% of fatty and waxy substances are contained in grape husks, according to S. Fachini and G. B. Martinenghi (Olii minerali grassi e saponi, colori e vernici 18, 78-81). T. H. Barry (Industrial Chemist 163, 319-22) pointed out that "dammar wax" is really a resene which, when purified, is a brittle white solid with a melting point of about 200°.

In a study of the carotenoids of fresh-water algae, J. Tischer (Z.physiol. Chem. 252, 225-33) employed the technic of chromatographic separation to obtain an insight into the composition of pigmented waxes from Hamatococcus *pluvialis.* The presence of euglenarhodon palmitate and other esters of euglenarhodon and of hematoxanthin was demonstrated by this method. M. Umezu and T. Wagner-Jauregg (Biochem. Z. 298, 115-24) stated that a chemically bound wax is an essential component of the tubercle bacillus cell wall. The wax is liberated by hydrolysis with dilute acid or alkali. The immunological reactions of this wax were reported by M. Yamasaki (Juzenkaizasshi 39, No. 8-9; 40, No. 7; Japan Lit. Tuberk. Forsch. No. 5, 25-8).

#### SYNTHETIC WAXES AND WAX SUBSTITUTES

The preparation of the following wax-like substances was described by G. D. Graves (U. S. 2,118,506): the laurate of the monododecyl ether of ethylene glycol and the stearate of the monododecyl ether of diethylene glycol. The latter melts at 24°.

Resins or waxes are produced from N-substituted 2-pyridone- and quinoloneamides according to E. Haack and R. F. von Buddenbrock (U. S. 2,124,505). In an example, N-methyl-2-pyridonemethylimide is treated with benzoyl chloride. In a patent issued to the Deutsche Hydrierwerke A.-G. (Brit. 470,-849) condensation products resembling hard waxes are made by heating aliphatic hydroxy compounds of high molecular weight with boric acid in a stream of inert gas. The alcohols obtained by the reduction of carnauba wax are used in one example. According to W. A. Lazier (U. S. 2,109,844) waxy esters are prepared from material

such as coconut oil by hydrogenation in the presence of a mild alcohol-forming catalyst, the temperature being above 200° and the pressure over 13.5 atmospheres. Copper chromite is a suitable catalyst.

The I. G. Farbenindustrie A.-G. (Brit. 482,209) described wax-like compositions made by mixing chlorinated naphthalene with isobutylene, and R. J. Butz and R. C. Cantelo (U. S. 2,118,915) produced wax acids by the oxidation of paraffin at 105-120°, using a stream of air bubbling through the molten paraffin at a rate of 0.5 to 10 cu. ft. per hr. The oxidation is stopped before the acid value and saponification value exceed 70 and 125, respectively. The acids are separated with the aid of an aqueous solution of sodium hydroxide and acetone. W. Meyer (Seif-ensieder-Ztg. 65, 215-17, 238-9, 256-8, 277-8, 297-9, 317-9, 338-40) prepared a comprehensive review relating to the preparation of fat acids, fat alcohols and wax esters by the oxidation of hydrocarbons.

Polymerization products of cetyl acrylate have wax-like properties, according to Röhm & Haas A.-G. (*Fr.* 818,740). They may be employed in making insulators, safety glass, adhesives, coating compositions and impregnating agents for cloth and leather.

R. Bhattacharaya and B. S. Gidvani (London Shellac Research Bur. Tech. Paper No. 75, 14 pp.) esterified the hydroxy groups of shellac with various fat acids. With the higher saturated acids they produced wax-like esters which are claimed to be satisfactory for use in polishes and sizing compositions.

#### EXTRACTION, REFINING, BLEACHING AND COLORING

A laboratory apparatus for the solvent extraction of waxes was described by V. H. Roehrich (U. S.2,101,819). A process for separating waxes from fats by saponification was patented by Zschimmer and Schwarz chem. Fab. Dölau (Ger. 656,215). The mixture is treated in such a manner that only the fats are saponified, preferably with the aid of a fat-splitting catalyst. The fat acids liberated are converted into soaps and the waxes are recovered by filtering, centrifuging, compressing or decanting. It is claimed that the process is applicable to marine animal oils containing both fats and waxes.

In a process for refining estertype waxes, the acidity is neutralized with the aid of aliphatic or aralkyl amines such as ethylenediamine, trimethylamine, allylamine or benzylamine, according to patents issued to S. L. Langedijk and W. Coltof (U. S. 2,126,334) and to the N. V. de Bataafsche Petroleum Maatschappij (Brit. 478,930; Fr. 816,289; Fr. 822,176). This firm and W. Coltof also obtained a patent (Dutch 42,485) on a proccess for recovering mono- or dihydroxy-2-alkylamines used for refining waxes. A. O. Tischer (Brit. 475,070) purified vegetable waxes. and their fractions containing fatsoluble vitamins, by treatment with furfural.

Waxes are granulated by first emulsifying them and then diluting the emulsion and cooling it below the melting point of the wax, according to F. G. Gilder and F. W. Gilder & Co. Ltd. (*Brit.* 477,280).

The Eastman Kodak Co. (Fr. 812,734) claimed the use of the following wax antioxidants: hydroquinone, pyrogallol, p-aminophenol, benzyl-p-aminophenol, furfural and 1,2,4-,trihydroxybenzene. The antioxidants are added to the waxes before distillation. Additional antioxidants for preserving waxes during high-vacuum distillation, patented by K. C. D. Hickman (Brit. 480,885) are: hydroxy-2hydroquinone, pyrocatechol, amino-5-hydroxytoluene, p-hydroxyphenylmorpholine, dibenzyl-p-ami-1,5-dihydroxynaphthanophenol, lene and p,p-diaminodiphenylam-This same worker (Brit. ines. 479,802) described a short-path, high-vacuum distillation process for animal and vegetable waxes in which a dye is added to the mixture before distillation, a dye being chosen that will distil at the temperature of the fraction desired.

F. N. Pickett (U. S. 2,126,277) prepared a deodorized wax solvent by the dry distillation of vulcanized rubber.

Waxes may be bleached with organic peroxides according to a process patented by V. R. Kokatnur and O. S. Plantinga (U. S. 2,121,-545). The temperature is maintained below the decomposition point of the peroxide and sodium hydroxide is added as a precipitant for the mucilaginous impurities and as a neutralizing agent for the free acids. In another patent issued to these same workers (Brit. 477,-282), the precipitant may comprise a mineral acid or aluminum sulfate. The use of fullers earth or other absorbent, and blowing with superheated steam in vacuo, are also covered. J. S. Reichert, D. J. Campbell, W. S. Hinegardner and L. P. London (U. S. 2,113,433) described a method for bleaching ester-type waxes without destroying their properties, in which a hot emulsion of wax is treated with alkaline hydrogen peroxide. The hydrogen ion concentration of the mixture is carefully controlled. The method is suitable for bleaching waxes such as beeswax and the products may be used in cosmetics.

Dyes for coloring waxes were patented by J. G. McNally and J. B. Dickey (U. S. 2,108,824); K. Koeberle and O. Schlichting (U. S. 2,123,245); and the I. G. Farbenindustrie A.-G. (Brit. 471,112; 471,686; 480,162; Fr. 817,559; 818,184; 823,646).

# PHYSICAL, CHEMICAL AND BIOCHEMICAL PROPERTIES

Useful information on the melting points of binary and trinary wax mixtures was recorded by J. R. Koch, G. J. Hable and L. Wrangell (Ind. Eng. Chem. Anal. Ed. 10, 166-8). The following systems were investigated: paraffin-carnauba-beeswax; paraffin-candelillabeeswax: carnauba-beeswax-candelilla: carnauba-candelilla-Chinese insect: paraffin-candelilla-ozokerite; candelilla-beeswax-ozokerite; beeswax-montan-ozokerite; paraffin - montan - beeswax; paraffinparaffin-beesmontan-ozokerite; wax-ozokerite; and beeswax-candelilla-Chinese insect wax. Isothermals were plotted for the above mixtures and for the various dual combinations possible with the individual waxes. If the qualitative composition of a wax mixture is known, the graphs presented in this paper will assist in determining its approximate quantitative compostion. The authors point out that the graphs will also aid in the preparation of wax mixtures of any desired melting point. It is shown that a relatively small amount of carnauba wax is needed to raise the melting point of individual waxes or their mixtures, and that Chinese insect wax is the only other wax that approaches carnauba in this respect. The work indicates that waxes form true mixtures and not definite chemical compounds when melted together. An apparatus and method for determining melting points were developed.

C. L. Mantell and R. W. Allan (Ind. Eng. Chem. 30, 262-9) determined the solubility of five varieties of dammar resin and one sample of elemi resin in beeswax, carnauba wax and montan wax. They reported that, in general, the dammar resins are completely miscible with the waxes used and that a rise in melting point occurs in most instances. Elemi lowers the melting point of the waxes but lends plasticity to the mixture. R. W. Allan (Chemical Industries 42, 507-8) determined the combining temperatures, loss in weight on heating, and the melting points of 30 mixtures of natural waxes and resins and suggested possible uses for these wax-resin combinations.

The dielectric after-effect in solid nonconductors (including wax) was studied by G. M. Voglis (Z.Physik 109, 52-79). R. Kohlhaas (Z. Krist. 98, 418-38) made an xray investigation of single crystals of cetyl palmitate and palmitic dicetyl ether. In a study of the molecular rotation in the solid forms of cetyl alcohol, W. O. Baker and C. P. Smyth (J. Am. Chem. Soc. 60, 1229-36) disclosed that this compound shows rotation in the alpha form. A strong anomalous dispersion of the dielectric constant occurs at the same time. J. Marsden and J. H. Schulman (Trans. Faraday Soc. 34, 748-58) investigated the effect of electric forces in monolayers of cetyl alcohol. Derivatives of this alcohol were used by N. K. Adam and H. L. Shute (Ibid. 34, 758-65) in research on the anomalies in the surface tension of paraffin chain salts. A. Guyer, A. Bieler and E. Hardmier (Helv. Chim. Acta 20, 1462-7) decribed the preparation of halides from cetyl alcohol and, in Russia, A. A. Trapeznikov and P. Rehbinder (Compt. rend. acad. Sci. U. R. S. S. 18, 185-9 [in English]) conducted work on the plastic properties of monolayers of cetyl alcohol, cetyl stearate, cerotic acid, palmitic acid, ethyl palmitate, tripalmitin, oleic acid, triolein and cholesterol on water in which multivalent ions were dissolved.

P. Nèlis (*Compt. rend. soc. biol.* 127, 487-8; 1423-5; 128, 28-31) found that a mixture of lanolin and liquid petrolatum was decidedly bactericidal to numerous species of pathogenic bacteria, while M. v. Eisler and F. Gottdenken (Z. Immunitäts 92, 112-17) stated that lanolin lowers the toxicity of cobra venom to white mice. The latter investigators (Ibid. 90, 427-51) studied the inactivation of diptheria toxin by this same wax. According to H.-I. Kim (Tokyo Igk. Z. 50, 1005-33; Japan J. Med. Sci. IV, Pharmacol. 10, Abstracts 6), daily feeding of 5 gm. of lanolin to rabbits for 6 weeks caused typical aortic arteriosclerosis. R. Maccolini (Compt. rend. soc. biol. 127, 1068-71) investigated the production of antibodies in the rabbit after injection of Aertrycke's bacillus mixed with lanolin.

#### COMPOUNDS DERIVED FROM WAXES

H. A. el Mangouri (Biochem. J. 31, 1978-80) reported that ketones and keto alcohols present in waxes could be converted into hydrazones by boiling with an al-coholic solution of *p*-hydrazinobenzoic acid (cf. Chem. Abs. 30, 6029), using pyridine as a catalyst. The barium salts of these hydrazones were found to be insoluble in boiling methyl alcohol and accordingly could be separated from the other unsaponifiable constituents of the wax. The hydrazones were readily regenerated by treatment with formic or acetic acid, the yield being 75 to 80%. The method was applied to the separation of nonacosan-12-one from cabbageleaf wax, and to the preparation of coccervl alcohol.

In the production of high-molecular aliphatic alcohols, A. Guyer (U. S. 2,110,483) hydrogenated cetyl palmitate, coconut oil or sperm oil, using a temperature of 250-300° and a hydrogen pressure of 150-300 atmospheres. A catalyst composed of chromium or copper oxides, containing 1% of iron, was employed to obtain alcohols such as cetyl alcohol. S. J. Green (Can. 371,129) also produced higher alcohols by hydrogenating wax esters or their corresponding acids. He used a rapid stream of hydrogen at a pressure of 5-50 atmospheres, the alcohols being carried out of the reactor by a stream of hydrogen as soon as they are formed.

W. Grote, E. Hundsdörfer and J. Moos (U. S. 2,113,960) described a procedure for separating saturated and unsaturated components

from waxes. The material is dissolved in carbon disulfide and cooled to about -15° to precipitate the saturated component. A. F. Bowles (*Am. Dyestuff Reptr.* [Proc. Am. Assoc. Textile Chem. Colorists] P32-7) investigated the *o*-boric esters of sperm oil alcohols.

#### EMULSIFICATION

Numerous agents for emulsifying or dispersing waxes were described during the year. H. Schou (Brit. 478,697) proposed compositions obtained by polymerizing or oxidizing fats containing the glycerides of linolic, linoleic or linolenic acids, the products being mixed with soap (see also Chem. Abs. 16, 3517; 17, 1092, 1093). This worker (Brit. 472,086) also used condensation products of higher fatty acids and polysaccharides as emulsifying and stabilizing agents for aqueous wax dispersions. Röhm & Haas Co. (Brit. 470,636) employed phenolic aralkylamino alcohols; H. J. Barrett (U. S. 2,-109,877) claimed the use of agents formed by the partial alcoholysis of polymeric esters of acrylic acids; and the duPont Co. (Brit. 475,132) patented the use of polymerized acrylic acid derivatives such as:  $\beta$ -dimethylaminoethyl methacrylate, 2-(diethylamino) cyclohexyl methacrylate, and  $\beta$ -morpholine-Nethyl methacrylate, polymerized in solution with the aid of benzovl peroxide. The Deutsche Hydrierwerke A.-G. (Brit. 483,324) prepared a wax dispersing agent by heating dodecylamine and betaine with phosphorus trichloride in the presence of pyridine and toluene. This same firm (Brit. 473,550) made stable emulsions of wax-like substances with the aid of a resin alcohol. In an example 50 parts of saturated alcohols obtained by reducing beeswax, 45 parts of mixed saturated alcohols of 14, 16 and 18 C atoms, and 55 parts of resin alcohols prepared by hydrogenating rosin are mixed with double the quantity of water and the whole is emulsified in a suitable machine.

C. Fostiropol and R. Verona (Fr. 824,390) produced emulsions from finely powdered waxes by first emulsifying the wax and incorporating a "water-fixing" substance, such as calcium oxide, which precipitates the entire mass in the form of an extremely fine powder.

Storage-stable wax emulsions, suitable for shoe creams, are pre-

pared by adding one of the following classes of compounds to the emulsion: peroxides, perborates, percarbonates, persulfates, and the alkali metal salts of nitrobenzoic, nitronaphthalic or nitrobenzenesulfonic acids. The process was patented by K. Behringer (U. S. 2.-128,025). A. W. Baldwin and H. A. Piggott (U. S. 2,100,297) claimed the use of the mercaptans of cetyl, ceryl and melissyl alcohols as stabilizers for wax emulsions.

#### ANALYSIS

M. A. Coler (Ind. Eng. Chem., Anal. Ed. 10, 164-5) devised a new method for determining the melting point of waxes. A small piece of the sample was affixed to the bulb of a thermometer. This was then immersed in a mercury bath which was heated at a constant rate. The temperature at which the material arose to the surface of the mercury was called the melting point.

The following method for the determination of free alkali in colored wax emulsions was developed by K. S. Nitsche (Ole, Fette, Waschse, Seife, Kosmetik 1938, No. 6, 1-3): Heat a 5 to 10 gm. sample of wax emulsion (leather dressing, shoe polish, etc.) with 50 cc. of water and add salt. After the solution clarifies filter and wash the precipitate with salt solution. Determine the carbonate alkali by any standard method in which carbon dioxide is liberated by hydrochloric acid. When alkali hydroxides are present prepare a separate salt solution extract, blow it with carbon dioxide and determine the amount of carbonate formed. Calculate the free alkali from the difference in the two determinations

G. Buchner (*Fette u. Seifen 44*, 518-19) discussed the possibility of variations in the analytical characteristics of waxes of the same type.

#### INDUSTRIAL USES

Polishing and Floor Wax Compositions

The Deutsche Hydrierwerke A.-G. (*Brit.* 473,551) described a shoe polish made from montan wax, the montanic ester of a dammar resin alcohol, ceresin, paraffin, turpentine oil, fat-soluble dye and solvent naptha. The same firm (*Brit.* 468, 533) proposed a polishing wax made from an ester of 1, 6-hexanediol, montan wax, ozokerite, paraffin and solvent naptha. A cleaning and polishing composition developed by A. Schwab (*Swiss* 193,031) contained kaolin, paraffin, beeswax and textile waste, and M. Martinoli (Swiss 192,157) prepared a mixture of wax, turpentine, sodium hydroxide, benzene and hydrochloric acid for use as a polish for linoleum, wood or tiles. I. Baranyai (Hung. 118,494) added alkaline pyrogallol solution emulsified with glycerol, together with casein, to the usual ingredients of shoe creams. It was claimed that such additions prevent early drying of the creams during storage.

J. D. Pickens (U. S. 2,118,521) claimed a solution of carnauba wax in mineral spirits, to which 1 to 6% of lauryl acid phthalate is added, as a liquid wax for polishing various coated surfaces. A composition for polishing floors, furniture, boots, etc., composed of barium stearate, paraffin and hard wax, was patented by H. Deguide (U. S. 2,126,096). The mixture is dispersed colloidally to form a gel.

The use of morpholine in wax polishes was discussed by H. F. Robertson and A. L. Wilson (Soap (Sanitary Products Sect.) 14, No. 9, 99, 101, 111; Chemical Industries 43, 290-2). In the latter reference the microscopic examination of morpholine polishes is described. V. Defelice (Bol. informaciones petroleras (Buenos Aires) 14, No. 156, 89-99) included the use of paraffin in floor waxes in a discussion of the industrial applications of this material.

The formulation of shoe polishes and creams was reviewed by G. S. Collingridge (*Chem. Age* (London) 39, 3-5), G. F. Caley (*Manuf. Chemist* 9, 7-8) and by L. Ivanovsky (*Seifensieder-Ztg.* 64, 650, 693-4, 715-16, 734-5, 754-5, 773-4, 793).

G. Gehm (Ibid. 64, 673-5) investigated the gloss and slipperiness of waxed linoleum floors in relation to external influences and the composition of the wax. He found that the use of 4 to 10% carnauba wax in floor wax having a total wax content of 30% gave a readily applied product. This had better gloss and much less slipperiness than similar compositions containing larger amounts of paraffin. Floor wax compositions were reviewed by G. S. Collingridge (Chem. Age (London, 37, 287-9), C. A. Tyler (Soap (Sanitary Products Sect.) 14, No. 4, 103, 105, 107, 115) and by J. C. Booser (Ibid. 14, No. 5, 99-101, 127). The latter reference comprises a discussion of floor wax specifications.

A general review of wax-containing products suitable for polishing, coloring and waxing wood, artificial resin articles and lacquered surfaces was compiled by L. Ivanovsky (*Farbe u. Lack* 1938, 29-30, 41-2, 55-6). A. Pollack (*Oberflächentech. 15*, 79-80) discussed the functions of the various binding agents in polishing pastes.

#### Molding, Plastic and Resinous Compositions

A composition for making phonograph record blanks was proposed by the Electrical Research Products Inc. (Brit. 473,459). In an example stearic acid and montan wax are heated together at 175° and a mixture of anhydrous sodium carbonate and basic lead carbonate is then added. After the reaction has subsided, a plasticizer (such as sperm oil) is mixed with the product. In another patent issued to this firm (Brit. 474,357) matrices for phonograph records are formed by sputtering gold onto a wax original and electroforming a matrix of copper on the gold. Bakelite G.m.b.H (Brit. 476,888) stated that spermaceti may be added to molding compositions prepared from phenol-aldehyde resins, and J. R. Morris (U. S. 2,123,543) formed milk bottle caps by diepressing a cellulosic material impregnated with wax, using high pressure. W. E. Herbert and A. R. F. Thompson (Proc. Roy. Soc. Med. 30, 245-62) employed a wax pattern in a method for the pressure-casting of gold alloy dental plates.

Phenol-ketone condensation products were hydrogenated to produce wax-blending agents by R. E. Thomas (U. S. 2,118,954) and H. Plauson (Brit. 472,228) described wax-like compositions for use in resinous condensation products. W. O. Herrmann and W. Haehnel (U. S. 2,127,381) obtained a product with increased hardness by using waxes with polymerized vinyl compounds. A wax, such as beeswax or carnauba, was added to esters of acrylic and itaconic acids, or esters of vinyl alcohols and styrene, and a solution of the mixture was polymerized. A similar patent was granted to the Chemische Forschungsgesellschaft m.b.H. (Brit. 469,319). This firm also stated (Brit. 469,976) that waxes may be used as addition ingredients in polymerization products derived from 2-chloro-1, 3butadiene. Henkel & Cie G.m.b.H.

#### oil & soap

(Brit. 475,549) caused phenol to react with aliphatic olefines in the presence of perchloric acid and then added formaldehyde. Waxes were added to the reaction mixture and the products were proposed for use in lacquers, as softening or film-forming agents and as adhe-sives. L. d' Antal (Brit. 483,907) added montan wax to sulfonated products of bituminous substances (such as montan pitch) to produce plastic masses. The I. G. Farbenindustrie A.-G. (Brit. 474,601; Fr. 819,394) prepared condensation products from diethylenetriamine or triethylenetetramine and montanic acid together with formaldehyde. It is claimed that such products are suitable for blending with waxes. Synthetic resins were made by the Deutsche Hydrierwerke A.-G. (Fr. 823,355) by condensing resin alcohols with phenols, aldehydes or ketones and adding waxes.

#### Waterproofing, Sealing and Coating Compositions

M. H. Belloc (U. S. 2,115,797) claimed the use of a vinyl resin, to which a small amount of natural or synthetic wax was added, for waterproofing paper, textiles and regenerated cellulose. J. V. Nevin (Brit. 470,772) used waxes for waterproofing an artificial wood prepared from sawdust and synthetic resin, and a patent granted to British Cellophane Ltd. (Brit. 472,264) described the use of wax to improve the water resistance of cellulosic sheets and films. A wax emulsion was employed by H. R. Dalton (Brit, 482,225) in a process for making moistureproof gummed tape, and A. Halward (Austrian 153,821) suggested the use of a wax emulsion containing casein for sizing or waterproofing fibrous materials.

The following patents pertain to the use of waxes or wax derivatives for making or coating transparent wrapping tissue: W. H. Charch, M. M. Brubaker and F. M. Meigs (U. S. 2,098,536); M. M. Brubaker (U. S. 2,100,377); R. T. K. Cornwell (U. S. 2,121,023); V. H. Wilshire (U. S. 2,123,760); D. C. Ellsworth (U. S. 2,123,883); C. M. Connor (U. S. 2,128,739); R. Koepp & Co. (Brit. 469,637); R. C. Allder, H. W. Hutchings and British Waxed Wrappings Ltd. (Brit. 471,544); T. G. Finzel (Can. 369,-101); J. A. Mitchell (Can. 370,-750); M. M. Brubaker (Can. 373,-630); H. Bradshaw (Can. 370,-735); and Sylvania Industrial Corp. (*Ger.* 663,139). Cetyl alcohol was found to be satisfactory as a softening agent in a process for waterproofing cellophane by K. Kanamaru, A. Shiratori and T. Nakamura (*Kolloid Z.* 84, 323-34).

A dispersion of wax in rubber latex was dried and employed for sealing cans by the Dewey & Almy Chem. Co. (Ger. 650,371) and E. L. Baldeschweiler (U. S. 2,131,-342) proposed a polymer obtained from isobutylene, plasticized with wax, for caulking and sealing joints and crevices. An adhesive for sticking insulating compositions to damp surfaces was described by the I. G. Farbenindustrie A.-G., K. Daimler and H. Thron (Ger. 651,-796). The product was prepared by heating wool fat with an aluminum salt above 100°.

Coating and impregnating compositions may be made by blending urea-aldehyde condensation products with waxes, according to the duPont Company (Brit. 483,399). A patent was issued to the I. G. Farbenindustrie A.-G. (Fr. 47,670addn. to 788,840) covering the use of beeswax or synthetic wax for coating electrolytic cells made from cardboard, asbestos, etc. The Soc. anon. des anciens ètablissements Martin Frères (Fr. 826,704) proposed an impermeable coating material prepared from pitch, oil, magnesium resinate and fiber wax.

C. M. Albion (U. S. 2,128,392) used a mixture of wax, chlorinated lime and borax as a fireproofing composition for roofing and electric insulation. J. R. Geigy A.-G. (*Brit.* 486,009) described a product for surfacing roads or floors, composed of bitumen and waxes.

Beeswax was employed in a transparent coating for light-sensitive devices by G. W. Hewitt (U. S. 2,104,483). Patents relating to the use of waxes for coating photographic materials were issued to E. J. Ward (*Brit.* 468,678) and Gevaert Photo-Producten N. V. (*Brit.* 481,702).

The following patents pertain to the use of waxes as resists in glassetching processes: Askania-Werke A.-G. vormals Centralwerkstatt Dessau and C. Bamberg-Fridenau (*Brit.* 480,918); Corning Glass Works (*Fr.* 814,427); Kodak A.-G. (*Ger.* 660,662); and Balog Ferenc ès Társa, etc. and I. Forgó (*Hung.* 117,241).

J. G. Weeldenburg (U. S. 2,100,-581) coated rayon spinnerets with a wax-like material to prevent the

formation of deposits around the orifice in the spinning operation. L. E. Beitler (U. S. 2,119,901) employed a coating of molten wax in a process for making gelatin caps for sealing bottles. A waxy material dissolved in a solvent was proposed for coating citrus fruits by R. Holzcker (U. S. 2,119,915), and G. Kereszty (Hung. 117,459) used a wax coating to protect cakes of saponifying agents from the atmosphere.

#### Emulsifying, Dispersing and Wetting Agents

L. Orthner and H. Keppler (U. S. 2,098,551) prepared wetting and dispersing agents by treating an ester-type wax such as beeswax with ammonia, primary or secondary aliphatic, cycloaliphatic, araliphatic or aromatic amines, polyalkene-polyamines or piperidine.

Sulphonated cetyl alcohol or the sodium salts of cetyl, oleyl and stearyl sulfates, which may be derived from sperm oil, were proposed as wetting, emulsifying and cleansing agents by H. Bertsch (U. S. 2,114,042; 2,114,043). Antifoaming and antifreezing solutions were made from montan wax or the esterification products of montanic acid by M. T. Flaxman (U. S. 2,127,490; 2,127,491).

A. Ofner (*Brit.* 468,956) mixed hexahydrobenzene or decahydronaphthalene with sulfonated cetyl alcohol to produce wetting agents. A patent issued to the I. G. Farbenindustrie A.-G. (*Brit.* 474,671) related to the preparation of wetting, foaming, dispersing, washing and dressing agents from quaternary ammonium compounds and cetyl alcohol or montanic acid. Reaction products from amines and cetyl alcohol were also described by C. Barbieri (*Brit.* 482,008).

The Soc. pour l'ind. chim. à Bâle (Fr. 822,058) obtained washing, dispersing and softening agents by esterifying cetyl alcohol with sulfocarboxylic acids, and the same firm (Swiss 193,075) described a washing and wetting agent derived from cetyl alcohol and a carboxylic acid amide. Henkel & Cie G.m.b.H. (Fr. 823,154) made a detergent from the sodium salt of whale oil, the sodium salt of a substituted cresoxyacetic acid and wool fat. Wetting agents were prepared by S. Z. Perlmuteer (Fr. 826,299) from a mixture of palm, olive and sperm oils, followed by sulfonation.

#### june, 1939 -

#### Cosmetic and Soap Industry

T. W. Deakers (Drug Cosmetic Ind. 43, 39-40,42) discussed the stability of creams and stated that, in the case of liquid beeswax-borax emulsions, better stability can be secured by adding castile soap or quince mucilage. Emulsifying agents such as glycol stearate or oleate are also useful. Water-inoil emulsions may become unstable if improper waxes are chosen as hardening agents. B. Fantus, A. Bachem and H. Dyniewicz (Merck Report 47, 17) suggested the following total sun-screen ointment; calamine 15, anhydrous lanolin 12.5, yellow petrolatum 37.5 and stronger rose water to make 100 gm. According to G. W. Fiero and L. D. Lockie (J. Am. Pharm. Assoc. 27, 402-4) cosmetic creams prepared with hydrogenated castor oil are stiffer than those made with white beeswax or spermaceti. They also stated that a mixture of equal parts of hydrogenated castor oil and white wax or spermaceti has a greater hardening power than any of these products used alone. Employing a mixture of equal parts of the hydrogenated oil and wax permits a 40% reduction of solidifier content of cold creams.

F. Factor and P. E. Fisher (U. S. 2,101,843) prepared a colored make-up cosmetic with the aid of waxes and H. Goodman (U. S. 2,129,836) used lanolin as a base in creams. C. Ellis (U. S. 2,128,-083) described a soap made from wax acids and the spent alkali solutions from petroelum refining, while L. F. W. Pape and H. Umbach (U. S. 2,105,366) proposed montan wax and wool fat as superfatting agents in liquid potash soaps.

According to E. V. Hayes-Gratze (Brit. 470,699) toilet preparations may be prepared by adding higher alcohols, wool fat or waxes to silica gel suspensions. N. V. S. Knibbs (Brit. 472,745) developed a hair-waving solution in which wax was used. A. Welter (Brit. 473,-220) made a stable powdered or molded soap with the aid of wax. A skin cream containing cetyl alcohol was patented by the Deutsche Hydrierwerke A.-G. (Brit. 473,-550), and the I. G. Farbenindustrie A.-G. (Brit. 474,476) prepared soaps by saponifying waxes and sperm oil and then removing the unsaponifiable portion by distillation and solvent extraction. P. M. Weinholdt (*Brit.* 478,176) employed beeswax in the manufacture of an adhesive depilatory. Compositions for controlling perspiration, containing alcohols, an astringent and small amounts of natural or synthetic wax, were described by W. C. Moore (*Brit.* 480,379).

A washing agent for the body, prepared from the sodium sulfonate of cetyl alcohol, colloidal kaolin and gum tragacanth, was patented by I. Reichstein (Fr. 819,633). A shaving cream containing wax was described by G. P. A. Brossard (Fr. 813,857), and L. Gresset (Fr. 814,010) used a wax in making rejuvenating compositions for the skin. According to F. Schmocker (Swiss 193,628) a toilet soap is prepared by mixing cetyl alcohol with the fat acids of hydrogenated castor oil. A composition for preventing sunburn was described by E. Merck chem. Fab. and A. Jordan (Ger. 652,925). It contained benzalacetone and wax.

The following reviews and discussions relate to the use of waxes in cosmetics: M. G. de Navarre (Am. Perfumer 36, 40; 37, 50; Mfg. Perfumer 3, 277), J. Kalish (Drug Cosmetic Ind. 41, 492-3, 506, 630-2), H. Hilfer (Ibid. 42, 446-7, 450); Anon. (Ibid. 43, 115), Anon. (Drug Trade News 13, No. 20, 53), R. A. Kramer (Ibid. 13, No. 13, 33), E. Bourdet (Rev. marques parfum. savon. 14, 179-80, 206-7, 280-2; 16, 20, 102-3), S. P. Jannaway (Perf. Essential Oil Record 28, 316), Anon. (Ibid. 29, 187), J. Augustin (Reichstoffind. 13, 168; Der Perfumer 12, 535; Seifensieder-Ztg. 65, 535-6), H. Janistyn (Der Perfumer 12, 494, 515, 595; Seifensieder-Ztg. 65, 660), W. Gänssle (Fette u. Seifen 44, 460-2), B. Filmer (Ibid. 45, 105-6), T. Naruse (Japan J. Dermatol. Urol. 41, 170), E. Ohlsson (Progressive Perfumery & Cosmetics July 1938, 66) and A. I. Naimark (Masloboino Zhirovoe Delo 13, No. 5, 30-1).

#### Pharmaceutical Industry

M. Schubert (Dermatol. Wochschr. 105, 1251) studied the use of lanolin-base ointments for healing wounds and the Lakeland Foundation (Brit. 486,847) developed a bactericidal salve containing water-soluble chlorophyll and

lanolin. According to R. O. Craw and C. O. Lee (Pharm. Arch. 9, 16 pp.) 2% of phenol has no antiseptic value in an ointment made with a lanolin base. J. R. Driver, G. W. Brinkley and M. Sullivan (Urol. Cutaneous Rev. 42, 587-92) treated indolent ulcers with an ointment made from 88% commercial cod liver oil and 12% of white wax. E. W. Lazell (Med. Bull. Veterans Admin. 14, 216-19) found that lanolin containing 10% of sodium oleate made an effective ointment for the treatment of acute ivy poisoning and eczema.

M. Brockman Chemische Fabrik (*Ger.* 655,934) described a waterfree solid cod liver oil which was prepared by heating the oil with a small amount of carnauba wax and/or ceresin. Other ingredients may be added.

For the treatment of syphilis, P. L. Salzberg (U. S. 2,110,473) recommended bismuth salts of monoalkyl polycarboxylates obtained by treating a bismuth nitrate solution with a dilute solution of an acid ester of cetyl or melissyl alcohols. The alcohols derived from the hydrogenation of sperm oil may be employed also.

Methyldihydrotestos t e r o n e, a synthetic male sex hormone, is activated by beeswax, probably because of its physical properties, according to studies conducted by S. Ugami and S. Susuki (Bull. Inst. Phys. Chem. Research [Tokyo] 16, 1464).

A stabilized hydrogen peroxide preparation that can be used in making antiseptic tablets was described by A. Reiche (U. S. 2, 120, -430). A wax or higher alcohols such as wool fat alcohols are used in the process. J. T. Goorley and C. O. Lee (J. Am. Pharm. Assoc. 27, 379-84) stated that waxes are not as satisfactory as shellac or shellac-castor oil as enteric coatings for pills. G. C. Gualdoni (Boll. chim. farm. 77, 373-9) added white wax to cocoa butter suppositories. This allows the incorporation of about 30% of chloral hydrate in the excipient.

A surgical adhesive tape, prepared with the aid of a wax emulsion was described by E. H. Nollau and D. A. Rankin (*Can.* 374,847). The use of spermaceti in pharmacy was reviewed by H. P. Kaufmann (*Fette u. Seifen* 45, 94-104).

#### oil & soap

#### Insecticides and Disinfectants

Cetyl alcohol was employed by V. Voorhees (U. S. 2,096,947) in an insecticidal oil spray for citrus or deciduous foliage. The following compounds were proposed as insecticides by A. K. Epstein and B. R. Harris (U. S. 2,123,186): cetyl ethylene glycol cyanopropionate, melissic acid monoester of sorbitol monothiocyanoacetate, cetyl thiocyano acetate and similar compounds.

The I. G. Farbenindustrie A.-G. (*Brit.* 473,592; *Fr.* 815,972) added wax to an insect repellant containing coumarin, and O. Stefanovic (*Fr.* 826,327) used as disinfectants the esters of beeswax alcohols with numerous inorganic acids. A dry disinfectant, made from wool fat and compounds of mercury or copper, was proposed by F. Wolff (U. S. 2,109,143).

#### **Electrical Industry**

E. E. Halls (Ice and Cold Storage 40, 163-4) discussed the wax impregnation of electrical equipment such as condensers. The parts are completely dried in a vacuum and the molten wax is introduced without breaking the vacuum. The same writer (Rubber J. 95, 477-9, 484) describe a wax composition for finishing electrical ebonite. A permanent high-insulation seal which is vacuum-tight can be made from ebonite dipped in wax, according to R. D. Bradfield (Can. J. Research 16, A, No. 3, 76). The waxes used in the electrical industry were considered by L. McCulloch (Elec. J. 35, 281-3). G. Fodor (Brit. 471,176) prepared a dielectric material for condensers by impregnating a layer of magnesium hydroxide with wax.

A mixture of resin, powdered glass and wax was employed by S. Bloomenthal (U. S. 2,111,742) for making electrical resistances. E. Studt (U. S. 2,122,118) proposed a composition of rubber, balata and wax for insulating joints in submarine cables. Beeswax was used in the manufacture of dielectric members for television transmitters by the Standard Telephones and Cables Ltd. (Brit. 474,591), and the Chloride Electrical Storage Co. Ltd. (Brit. 479,390) described an emulsion of waxy substances and bentonite for making porous separators for electric batteries. The Western Electric Co. (Brit. 479,392) added 5% of a vegetable wax, such as carnauba or candelilla, to an asphaltic composition used to surround a condenser which has been impregnated with a halogenated hydrocarbon. S. G. Hale and C. D. Owens (*Brit.* 481,249) insulated magnetic cores for inductances by dipping the cores in molten "Superla" wax, and Bakelite Ltd. (*Brit.* 482,206) added carnauba wax to the outside coating composition of an insulating material made from varnished cambric.

#### Metallurgical Industry

Chromate-pigmented lanolin gave satisfactory protection to steel exposed one year to intermittent saltwater spray and marine exposure, according to H. Sutton and C. Braithwaite (*Iron Steel Inst.* [London], Special Rept. No. 21, 397-420).

D. T. May (U. S. 2,098,300) employed a protective coating of wax in a process for the electric welding of metallic tapes and ribbons. H. Libovitz, W. Mueller and W. Pfeiffer (U. S. 2,129,377) prepared the following composition for polishing hard metals: silicious earth 1250, aluminum oxide 750, powdered tripoli 250, petroleum jelly 250, ceresin 125, stearic acid 125, montan wax 50, cotton waste 25-250 and tar or asphalt 25-250 parts. Schering-Kahlbaum A.-G. (Brit. 469,571) coated aluminum or its alloys electrolytically and then immersed the coated articles in molten wax, and Robert Bosch A.-G. (Fr. 821,048), in a process for coating surfaces by treatment with metal vapors, used a wax film to protect the parts not requiring a metallic coat. The process is applicable to the manufacture of metallized paper for use in electrical apparatus and for making motion picture films and sound-film records.

#### Petroleum Industry (Including Lubricants)

C. D. Barnes and M. Flaxman (U. S. 2,119,938) added oxidized lanolin to aid wax separation in the liquid propane method of refining lubricating oil stock. E. F. Pevere (U. S. 2,100,915) used cetyl alcohol fatty esters and the Texaco Development Corp. (Brit. 482,327; Fr. 812,430) suggested a mixture of crude montan wax and aluminum stearate as modifiers in the dewaxing of mineral oils. In another process for dewaxing oils, M. L. Wade (U. S. 2,107,771; 2,107,-772) employed montanic, melissic and cerotic acids or beeswax, montan or carnauba waxes as electrodeposition accelerators, while W. B. Hendrey and E. C. Knowles (*Can.* 371,685) proposed the addition of 0.1-1.0% of a mixture of montan wax and metallic soap.

About 2% of cetyl alcohol inhibits the oxidation of lubricating oils according to R. W. Richardson and J. J. Owen (U. S. 2,119,114), and B. H. Lincoln and A. Hendriksen (U. S. 2,109,357) found that chlorinated carnauba wax increases the film strength of such oils. R. Kobayashi (J. Fuel Soc. Japan 16, 91-100) stated that the addition of 0.5-1% of solid waxes prevents "freezing" of lubricating oils.

A lubricant was made by voltolization of spermaceti oil by the Standard Oil Development Co. (Fr. 815,962). An anti-rust composition and lubricant can be prepared by sulfonating a mixture of chlorinated wax and an aromatic hydrocarbon and blending the product with asbestos, wax and graphite, according to F. H. MacLaren and L. C. Brunstrum (Can. 375,-Anti-corrosive lubricants 825). suitable for rock drills were de-scribed by C. C. Wakefield & Co. Ltd. (*Brit.* 469,889). In an example mineral oil 90, wool wax 10, lead oleate 0.25 and chromium oleate 0.10% comprised the lubricant. The Standard Oil Development Co. (Fr. 822,789) patented a lubricant for precision instruments, prepared from tritolyl phosphate, glycol phthalate and spermaceti oil.

P. A. Rebinder and E. K. Venstrem (Bull. acad. sci. U. R. S. S., Classe sci. nat., Sér. phys. 1937, 531-48 (in German 548-50) found that the addition of small amounts of surface active substances, such as cetyl alcohol and cerotic acid, to paraffin oil greatly facilitated plastic deformation of lead, tin, and copper in the form of wire or sheets. Extreme pressure lubricants were discussed by E. A. Evans (Inst. Mech. Eng., Lubrication dis-cussion, Oct. 1937, Group III, 48-52). Almost all of the mineral oil films have a rupture strength of 4,000 to 5,000 lbs. per sq. in. The liquid waxes and fatty oils vary from 8,000 lbs. for sperm oil to 15,000 lbs. for rape oil. R. C. Williams and Ironsides Co. (Brit. 473,056) made an extreme pressure lubricant from emulsified candelilla wax.

A cup grease stabilized with 1 to 8% of cetyl alcohol was patented by L. C. Brunstrum and E. W. Adams (U. S. 2,108,643). These same workers produced a lubricant

for plug valves by condensing an aromatic hydrocarbon with a chlorinated wax (U. S. 2,119,522; 2,-119,552). I. Hall (Brit. 469,012) developed a stick lubricant encased in a tearable lead sheath. The composition used was made from Japan wax (tallow) containing small quantities of paraffin, carnauba wax, beeswax and 5 to 20% of ammonium chloride. According to T. H. Thompson (Brit. 473,314) a mixture of paraffin, carnauba wax and hydrolene is suitable for impregnating leaf spring liners, and G. Snoek (Fr. 827,095) prepared solid or semi-solid lubricating compositions from cetyl alcohol.

#### Paper Industry

In a process for making waxed paper, A. Potdevin (U. S. 2,097,-601) passed a continuous web through a bath of molten wax and then cooled the product in a bath of water. An aqueous wax emulsion was employed by L. L. Dodge (U. S. 2,099,726) to increase the transparency of paper. Processes for making transparent paper, involving the use of natural and synthetic waxes, were devised by T. G. Finzel and D. E. Drew (U.S, 2,108,806; 2,108,809; 2,108,810). Instead of using ink in self-recording instruments, Winkelmann (Feuerungstech. 25, 302-3) recommended a stylus for tracing fine lines on waxed paper. Methods for sizing paper with waxes were described by R. W. Allan (Chem. Industries 42, 507-8 and by H. Hentschel (Zellstoff u. Papier 18, 456-62, 519-21; Wochbl. Papier-fabr. 69, Tech. Tl. 589-92).

According to J. Seiberlich (Pa-per Trade J. 107, No. 3, 41-2), paper bags may be satisfactorily waterproofed by coating them with a very thin film of a mixture prepared from carnauba wax 5, ceresin 5, petrolatum 10 and rosin 5 parts. A brush coater was especially designed for this process. The British Titan Products Co. Ltd. (Brit. 471,827) impregnated paper, cardboard and fiberboard with nonaqueous suspensions of titanium pigments in thermoplastic materials such as natural or artificial waxes. A dispersing agent was employed. V. H. Wilshire (U. S. 2,123,760) described a pliable, waterproof laminated paper prepared with the aid of wax, and F. Ohl (Wochbl. Papierfabr. 69, Tech. Tl. 193-6) gave a number of recipes for the use of synthetic waxes in the paper, carton and board industries.

C. S. Hamersley and S. C. Fairbanks (U. S. 2,099,301) devised a waxed paper wrapper for loaves of bread, the edges of the wrapper being coated with a resinous adhesive. A paper sizing composition, made from brown wax with petroleum oil as a softening agent, was proposed by C. Ellis (U. S. 2,099,-880), and waxed paper was employed to coat insulating material for building walls by R. W. Mc-Laughlin Jr. (U. S. 2,113,068). W. H. Brice (U. S. 2,118,152) employed a mixture of wax and resin for rendering wrapping paper resistant to moisture and vapor.

Other patents covering the manufacture and use of waxed paper were issued to the following: S. Musher (*Brit.* 477,386); The Institute of Paper Chemistry (*Brit.* 480,097); G. J. Manson (*Can.* 372,256); W. Gebhardt (*Fr.* 811,-984); Paterson Parchment Paper Co. (*Fr.* 812,504); I. G. Farbenindustrie A.-G. (*Fr.* 824,952); Schoeller & Hoesch G.m.b.H. (*Ger.* 652,124; 652,491); and Titan Co. Inc. (*Ger.* 657,599).

#### **Textile Industry**

In a discussion of methods for waterproofing textiles, R. Lindenmaier (Am. Dyestuff Reptr. 27 (Proc. Am. Assoc. Textile Chem. Colorists), P286-9) stated that wax emulsions containing either aluminum formate or acetate as the fixative are now employed. L. Billings (Ibid. 27, P265-9), F. B. Mc-Lain (Ibid. 27, 507-17) and A. Foulon (Allgem. Oel-u. Fett-Ztg. 34, 451-3) described the use of waxes for waterproofing.

F. Ohl (Ibid. 35, 58-61) related how montan wax and montan wax soaps were used in the textile industry. This same writer (Monatsh. Seide Kunstseide 43, 235-7) described the simultaneous use of naphthenic acids and their derivatives with waxes in textile finishing. L. Ivanovszky (Seifensieder-Ztg. 65, 327-8) stated that impregnation with an aluminum soap-wax emulsion does not prevent the rotting of hemp cords buried for 32 days in moist soil. E. Elöd and H. Rudolf (Klepzig's Textil-Z. 41, 295-8) found that treating wool with wool fat emulsions protects the fiber from damage during carbonization, but that staple rayon is not protected by this treatment. The emulsion likewise does not prevent damage to mixed fabric containing rayon during the mercerizing process.

Aqueous emulsions containing lanolin, paraffin and ilmenite were employed by P. W. Cunliffe (J. Textile Inst. 28, T341-8) for making a standard artificially soiled wool fabric.

E. A. Murphy and E. W. Madge (U. S. 2,096,753) prepared a showerproof fabric by treating gabardine with an aqueous dispersion of rubber and carnauba wax. A waxy substance such as diethylene-glycol stearate was used by C. Dreyfus and W. Whitehead (U. S. 2,127,-586) for coating pile fabrics,

Waxes may be added to a composition for making a semi-stiff material for collars and cuffs, according to the Deutsche Celluloid-Fabrik (Brit. 470,969). F. F. Swartz and M. A. Chavannes (Brit. 471,231) described the use of wax in the preparation of coated fabrics, and Ultrazell G.m.b.H. (Brit. 472,473) employed borax, spermaceti, dextrin, etc. in starching compositions. Solutions of waxes were used to impregnate fabrics in a method for producing pattern effects. The method was patented by Heberlein & Co. A.-G., G. Heberlein and E. Weiss (Brit. 473,069; addn. to 469,138). M. Blancato (Brit. 473,126) prepared emulsions of mineral, vegetable and animal waxes for preserving and waterproofing fabrics. A continuous process for coating fabrics with aqueous dispersions of synthetic resins and waxes was devised by G. C. Tyce, Imperial Chemical Industries Ltd. and V. Lefebure (Brit. 473,657), and the I. G. Farbenindustrie A.-G. (Brit. 474,601) described resinous compositions made from montan wax acids which can be used for waterproofing fabrics. Other resinous products made from waxes and used in treating textiles were developed by H. A. Piggott, F. S. Stratham and Imperial Chemical Industries Ltd. (Brit. 475,095).

The latter firm and G. W. Worrall (*Brit.* 475,737) employed a coating of wax to waterproof fabrics treated with a mixture containing rubber and sodium silicate. The Winterbottom Book Cloth Co. Ltd., G. E. Pilkington and T. L. Dale (*Brit.* 476,365) made a waterproof, translucent tracing cloth by padding cotton cloth with viscose mixed with an aqueous emulsion of beeswax.

A process for manufacturing adhesive fabrics, using a wax emulsion, was patented by the du Pont Co. (*Brit.* 479,111), and waterproof fabrics prepared with the aid of a dispersion of rubber, wax and soap were described by G. H. Ellis and E. Stanley (Brit. 481,610). Another process employing a dispersion of rubber and wax was patented by Rubber Producers Assoc., Wool Industries Assoc., B. H. Wilson and C. M. Blow (Brit. 483,496). Fibrous materials such as varns, fabrics and paper can be rot-proofed with the aid of a rosinwax size, according to National Processes Ltd. and W. J. Carter (Brit. 484,576). A. Prescher (Brit. 486,023) treated wool fibers with an aqueous emulsion of wool fat dispersed with a water-soluble cellulose ether, and the Warwick Chemical Co. (Brit. 485,398) recommended the use of sulfonated sperm oil to prevent the generation of static charges on silk or rayon.

Wax may be added to condensation products of abietic acid and glycerol to produce compositions for sizing threads, according to Etablissments G a m m a (S o c. anon.) (Fr. 812,662). The Chemische Fabrik Theod. Rotta and K. Quehl (Fr. 825,474) improved the weight, feel and elasticity of textiles by treating them with proteins and wax dispersions.

Glass filaments intended for use in the manufacture of textiles are first roughened by hydrofluoric acid and are then treated with an adhesive, such as a wax emulsion, in a process developed by Akt.-Ges. der Gerresheimer Glashüttenwerke vorm Ferd. Heye and L. Jansen (Ger. 663,006). Zschimmer & Schwarz chem. Fab. Dölau (Ger. 652,956) employed cetyl alcohol, partly esterified with phthalic acid, for waterproofing fabrics. An ester of cetyl alcohol with a complex phthalic acid derivative, intended for use as a textile dressing, was reported by the Soc. pour l'ind. chim. à Bâle (Swiss 194,944; addn. to 193,675).

#### Paint, Varnish and Lacquer Industry (Including Ink and Crayons)

The use of beeswax and possibly lanolin as vehicles for painting by the ancients was discussed by C. L. Burdick (*Tech. Studies Field Fine Arts 6*, 183-5) and the technic of picture relining with wax was described by S. Cursiter and A. Martin (*Ibid. 7*, 80-7). F. Ohl (*Seifensieder-Ztg. 65*, 48-9, 65-6) reported the composition of wax emulsions useful for staining wood.

A vegetable wax was employed by F. W. Humphner (U. S. 2,100,-

140) in a decalcomania composition and K. E. Crooks (U. S. 2,-104,637) developed a method for treating wood. According to the latter patent, a penetrating waterproof product made from tung oil is applied to wood and, after the material has dried, a coating of carnauba wax is applied from a solution. O. F. Gargen and C. J. Ernst (U. S. 2,125,237) prepared a polishing paint from lithopone, aluminum silicate, cooked linseed oil, flatting varnish and beeswax.

Pigments for enamels, lacquers, inks, etc. were ground in emulsions of natural or synthetic waxes by the du Pont Co. (Brit. 469,422). P. Lusseyran (Can. 374,235) prepared a titanium pigment suspension by adding the pigment to a molten mixture of wax and lanolin, the batch being agitated continuously. Paints or coatings may be made from aqueous dispersions polymerizates mixed with natof ural or synthetic waxes, according to the I. G. Farbenindustrie A.-G. (Fr. 819,147). A patent issued to the Vereenigd Industrieel Bezit Veritex N. V. (Fr. 820,695) described the lacquering of flexible materials with a coating of rubber and synthetic resin, a layer of nitrocellulose lacquer and finally a layer of wax. Titan Co. Inc., W. W. Plechner and J. M. Jarmus (Fr. 823,589) dispersed pigment particles in waxes and used a small amount of glycerol, triethanolamine, pentaerythritol or boric acid to prevent deposition. A paint and lacquer remover, containing rubber and a waxy material, was patented by Duco A.-G. (Ger. 655,454).

An ink suitable for manifold carbon papers was made from a mixture of wax, metal soaps, solvents and a cellulose ester by O. Weissberger and F. Polák (Brit. 473,496). R. A. Crawford (Can. 374,102) described a printing ink comprising liquefied rubber, ink black, petrolatum, montan wax and castor oil, and M. Schiffini (Fr. 827,775) prepared crayons by mixing colophony, stearin, yellow wax and chrome yellow.

#### Leather Industry

A polish for leather furniture may be made as follows: mix paraffin (m.p. 50-55°) 20, ceresin 5, neutral lanolin 5, beeswax 10, carnauba wax 10 and turpentine 50%. The desired amount of color is added. For preserving leather, the following formula is proposed: light petroleum jelly 62, paraffin 16, lanolin 10, ammonium sulfoicthyloate 7 and neatsfoot oil 5%, with birch tar oil as required. These recipes appeared in the *Industrial Chemist 14*, 416-7. Dressings and polishes for use on leather were described by F. v. Artus (*Seifensieder-Ztg. 65, 669-71, 693-*4).

O. Röhm (*Ger.* 651,992) treated sole leather with a hard wax, and wax compositions for improving the adhesion of driving belts were developed by the I. G. Farbenindustrie A.-G. (*Ger.* 655,008).

#### Rubber Industry

W. v. Denffer (*India Rubber World 98*, No. 3, 44-5) discussed the use of wax surfacing agents on rubber flooring, and H. J. Stern (*Rubber Age* (London) 18, 391-2) recommended the following composition for general use in marking uncured rubber mixes: montan wax 3, beeswax 1 and chrome yellow 3 parts. If the stock is to receive no further treatment, and if a mark that vanishes during vulcanization is desired, the following mixture should be used: montan wax 3, beeswax 1, zinc oxide 1 and dry white lead 1 part.

Montan wax was employed in a composition for making a rubber sand-blasting stencil sheet by A. J. Jennings (*U*. S. 2,098,748). G. Š. Hiers (U. S. 2,100,714) developed an unvulcanized non-tacky rubber product, such as rubber-treated pile fabric, by incorporating candelilla wax into the aqueous rubber dispersion used. P. J. Wentworth (U. S. 2,103,884) prepared a shoe filler composition by blending ground-up tire carcass with a rubber solution containing a waxlike material, the latter being employed to prevent contraction. Rubber-coated fabrics for auto tops were prepared from a composition containing 5 to 20% of wax by R. Morgan (U. S. 2,110,-070).

Softening agents for use with pigments employed for coloring rubber may comprise cetyl alcohol, spermaceti, beeswax or carnauba wax, according to Imperial Chemical Industries Ltd., M. Jones, W. F. Smith and A. Stewart (Brit. 438,192). Rubber derivatives were prepared by treating a rubber solution with a fluorine compound and blending the product with beeswax or carnauba wax. The method was patented by Rubber Producers Assoc., E. H. Farmer, H. P. Stevens and J. W. Rowe (Brit. 467,-531). The Dewey and Almy Chem. Co. (Brit. 477,210) described rub-

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ber gaskets containing a lubricant that does not soften the rubber. The lubricants mentioned are paraffin, beeswax, carnauba, candelilla, montan or Chinese insect waxes. Rubber halide films plasticized with spermaceti were produced by the Wingfoot Corp. (Brit. 479,464). Patents covering the use of a rubber-wax composition for making a coated sheet material were granted to the Marathon Paper Mills Co. (Brit. 481,-426; 481,427; 481,428). The Harvel Corp. (Brit. 481,960) added polymerized cashew nut shell oil to rubber compositions containing waxes.

#### Miscellaneous Uses

Recipes for nine ski waxes were given in the Industrial Chemist (14, 416-7) and L. Walden (School Sci. Rev. 19, 212-27) described the use of various waxes in the laboratory. Products useful as additions to wax preparations were patented by M. M. Brubaker and B. W. Howk (U. S. 2,100,-468) and by the I. G. Farbenindustrie A.-G. (Brit. 476,189). B. H. Porter (J. Applied Phys. 8, 47982) studied the impregnation of waxes with graphite.

Compositions that slowly evolve gases were described by J. M. Holm and Imperial Chemical Industries Ltd. (Brit. 477,956) and by H. H. Heer (Brit. 483,390; Fr. 813,103). Waxes were used in these products. P. Stock (Brit. 481,627) employed a wax mold in the manufacture of a transparent gas mask, and K. Braun (Ger. 659,874) developed a wax-coated filter for beer. A firelighter made from resin, hard wax, wax soap and petroleum was prepared by Martin Fiedler G.m.b.H. (Ger. 662,985). In a process for making ruled screens for photomechanical or optical purposes, H. Eckerlin (Brit. 471,703) used a resist varnish made from a solution of wax and asphalt.

O. R. Sweeney and L. K. Arnold (*Iowa State College Agr. Mech.* Arts, Eng. Expt. Sta., Bull. 136, 75 pp.) discussed the use of wax sizing in the manufacture of insulating board. Wool fat and wool fat pitch are used in making colored roofing compositions, according to C. R. Platzman (Farben-Ztg. 42, 436-7). M. F. Monbiot and British Rayophane Ltd. (Brit. 471,440) patented the following coating composition: a solution of chlorinated rubber 25-45, a resin 15-40, a plasticizer 15-25 and a wax 10-15%. The coating is used for textiles, paper, leather, wood and sheets of cellulose derivatives or gelatin.

or gelatin. C. Brooks (*Proc. Am. Soc. Hort. Sci.* 35, 720) reported that waxing the stem scar of tomatoes to delay ripening had about the same effect on flavor and quality as the delay caused by low temperatures. The use of lanolin preparations of growth-promoting substances was described by P. W. Zimmerman and A. E. Hitchcock (*Contrib. Boyce Thompson Inst.* 9, 299-328), N. Brown and F. E. G ardner (*Phytopathology* 27, 1110-13), and by J. W. Mitchell and C. L. Hamner (*Botan. Gaz.* 99, 569-83).

Progress in the production and use of waxes and wax-like substances was discussed by R. Straus (*Seifensieder-Ztg.* 65, 246a-247, 267-9).

## **ABSTRACTS**

# **Oils and Fats**

GERMAN FISH UTILIZATION. A Behre. Fette u. Seifen 46, 187-9 (1939).

GERMAN MODERN WHALING. N. Peters. Fette u. Seifen 46, 190-2 (1939). The I value of the blubber, bone and flesh fat of the blue whale, resp., were 121.8, 116.9 and 126.6; these values for the fin whale were 118, 112.5 and 131.6. The I value for the humpback whale oil of east Atlantic was 135, west Atlantic 138-140 and Indian Ocean 127-129. The I value of the oil from whales of the antarctic vary in some parts from 106 to 108 and from other parts from 123 to 126.

SENSITIVITY OF FISH LIVER OIL TO OXIDATION. H. P. Kaufmann and H. Fiedler. Fette u. Seifen 46, 200-3 (1939). Graphical and tabular data on the oxidation of 10 fish liver oils as detd. by the Mackey test are presented. It is possible that this test may be used in place of manometric  $O_2$  uptake methods.

USEFULNESS OF THE MACKEY TEST FOR JUDGING OLEINS. H. P. Kaufmann and H. Fiedler. Fette u. Seifen 46, 210-3 (1939). Oils with a difference greater than 20 between the I value and the SCN value give positive Mackey tests. Oleic acid prepns. contg. 1% Ni stearate of 0.1% Fe stearate, even though the difference in the above values is small give positive Mackey tests. Data on the influence of free fat acids, pro-oxidants, antioxidants and unsaponifiable on the course of oxidation are graphically presented.

#### Edited by M. M. PISKUR and RUTH LINDAHL

CHEMISTRY OF FAT SPOILAGE. VII. THE INFLUENCE OF HEATING ON THE STORAGE CAPACITY OF FAT. J. J. Köchling and K. Täufel. *Fette u. Seifen 46*, 206-9 (1939). Heating in air increases the susceptibility of an oil to oxidation and with heating in N<sub>2</sub> atmosphere the increases are in a lesser degree. Acceleration of oxidation of peanut oil was possible by adding 2 cc. of the heated oil to 15 cc. of unheated oil. Tabulated data show the degree of the effect on heating at different temps. and using oils in various stages of oxidation.

A NEW CHARACTERISTIC FOR OLIVE OIL. J. Grossfeld and H. Timm. Z. Untersuch. Lebensm. 77, 249-53 (1939). Fresh olive oils contain small amts. of highly unsatd. hydrocarbons that require considerably larger amts. of I than those hydrocarbons of other edible oils according to the Margosches I no. detn. Details for the method of sapong. the oil extg. the hydrocarbons with benzine and detg. I value are presented. The results are calcd. as the per cent Squalene in the oil. The data on fresh olive oils were 0.41-0.54% squalene; old olive oils, rape oil, peanut oils, sesame oil, linseed oil, apricot oil and train liver oil contained 0.02-0.10% squalene by the method. Dryng the hydrocarbons at 105° before detg. I value did not influence the results.

A RARE ADULTERANT OF OLIVE OIL. J. Pritzker and Rob. Jungkunz. Z. Untersuch. Lebensm. 77,