Edible Coatings from Morpholine-Free Wax Microemulsions

Robert D. Hagenmaier* and Robert A. Baker

Citrus and Subtropical Products Laboratory, Agricultural Research Service, U.S. Department of Agriculture, 600 Avenue S, N.W., P.O. Box 1909, Winter Haven, Florida 33883-1909

Edible wax coatings were made by the drying of wax microemulsions composed of water, fatty acid, ammonia, and various combinations of candelilla wax, beeswax, carnauba wax, polyethylene wax, and petroleum wax. All 19 coating formulations studied were effective moisture barriers, with the best being those containing candelilla wax, beeswax, and petroleum wax. Polyethylene and carnauba wax coatings had best gloss, but also were the most brittle. Emulsion clarity was improved by using some myristic or palmitic acid, rather than commercial grade oleic acid as the only source of fatty acid. Compared to wax coatings made with ammonia-based emulsions, those made with morpholine had higher permeability to oxygen and water vapor, possibly because the morpholine, being less volatile than ammonia, stayed longer in the coating.

Keywords: *Microemulsion; edible coating; edible; wax*

INTRODUCTION

Microemulsions are made up of two immiscible liquid phases with the discontinuous phase having globule diameter <0.2 μm. Because of this they appear clear or translucent and do not cream, unlike ordinary (macro)emulsions that appear white and usually form a cream layer (Prince, 1977). The first microemulsion made was a carnauba wax/oleic acid formulation made by Rodawald in 1928 (Prince, 1977). Hitz and Haut (1942) coated apples with "paraffin wax emulsified with ammonium linoleate"—quite possibly a "microemulsion", a name not coined until 16 years later (Prince, 1977). Wax coatings made by the drying of microemulsions have been shown to reduce weight loss from evaporation of water when applied to fresh fruit (Hagenmaier and Baker, 1995; Morales Guerrero et al., 1977), although their use as moisture barriers for other foods has not generally been explored. The reason for this is perhaps that those wax microemulsions used as fruit coatings generally contain morpholine, an ingredient permitted by the U.S. Food and Drug Administration (FDA) only in those edible coatings applied to the surface of fresh fruits and vegetables (21 CFR 172.235). Moreover, the formulations of wax microemulsions are generally proprietary, thus making it difficult for the food technologist to reformulate to exclude morpholine. The application of wax to foods as microemulsions makes it possible to apply a very thin coating to foods for which application of molten wax may not be appropriate.

The goal of the present work was to develop morpholine-free, wax microemulsion coatings that have general potential as edible coatings and to make public their formulations.

MATERIALS AND METHODS

Refined candelilla wax and carnauba wax NC 3 light flakes were obtained from Strahl & Pitsch Inc., West Babylon, NY. Beeswax was obtained from Koster Keunen, Inc., Sayville, NY. Petroleum wax was Parvan 161 from Exxon Corp., Houston, TX. Antifoam additive was a 10% emulsion of polydimethyl-

Table 1. Coating Formulations

sample	wax[b] components	fatty acids oleic (g)	palmitic (g)	myristic (g)
BW2	BW 100 g	0	12	12
BWCN2	BW 67 g, CN 33 g	0	22	0
BWCN3	BW 50 g, CN 50 g	11	11	0
BWCR3	BW 67 g, CR 33 g	0	11	11
CN2	CN 100 g	24	0	0
CN3	CN 100 g	12	4	0
CN4	CN 100 g	12	12	0
CR2	CR 100 g	0	11	11
CR3	CR 100 g	11	0	11
CR4	CR 100 g	0	0	24
CR5	CR 100 g	17	0	3
CRBW2	CR 60 g, BW 40 g	12	12	0
CRCN2	CR 50 g, CN 50 g	24	0	0
CRPV2	CR 50 g, PV 50 g	17	0	3
CRPV3	CR 75 g, PV 25 g	17	0	3
PE2	AC680 100 g	13	0	7
PE3	E20 100 g	0	0	18
PEPV2	AC680 75 g, PV 25 g	13	0	7
PEPV3	AC680 50 g, PV 50 g	6	6	6

[a] All also contain water to attain 20% total solids, 13.5 g of 30% NH_3 and 60 mg (dry basis) of polydimethylsiloxane antifoam. [b] BW, beeswax; CN, candelilla; CR, carnauba; PV, Parvan 161.

siloxane (FG-10, Dow Corning, Midland, MI). The fatty acid components (Table 1) were food grade, commercial preparations: the oleic acid preparation (82% oleic, 12% linoleic, 6% palmitic) was Palmac 760 (Condor Corp., Englewood Cliffs, NJ). The palmitic acid was Hystrene 9016 (92% palmitic, 7% stearic, 1% myristic); and the myristic acid preparation was Hystrene 9014 (90% myristic, 6% palmitic, 4% lauric), both from Humko Chemical Division, Witco Corp. (Memphis, TN).

Microemulsions were made in a closed, cylindrical reaction vessel (inside height 27 cm, radius 5 cm) stirred at 500 rpm with two propeller mixing blades, located at 2 and 7 cm from the bottom, heated by immersion in a water/ethylene glycol bath. Typically, about 150 g of wax, 30 g of fatty acid, 1 g of FG-10 antifoam, 21 g of 30% NH_3, and 75 g of water were heated in this vessel for 30 min at 20 °C above the melting point of the wax, and water (at approximately 95 °C) added at intervals of 1 min in three increments: 100, 100, and 500 mL. The reaction vessel was immersed in a cold water bath, with stirring continued until the temperature dropped to 50 °C. The contents were then poured out, diluted with water added to 20% total solids (determined by drying for 30 min at 140 °C), filtered through glass wool, and stored at room temperature in a covered container. The polydimethylsiloxane

* Author to whom correspondence should be addressed [telephone (941) 293-4133, ext 123; fax (941) 299-8678; e-mail BobHagmr@aol.com].

was used for the purpose of avoiding foam, but it may not have been necessary or even beneficial with all formulations.

The percent cream was calculated as the fraction of the nonvolatile solids found in the cream layer formed when the microemulsion (at 20% total solids) was centrifuged at 20 000 rpm for 15 min.

Turbidity was measured in nephelometer turbidity units (NTU) with the Hach Ratio/XR Turbidimeter (Hach Co., Loveland, CO). Samples (two replicates) were prepared by mixing water with emulsion to adjust solids content to 5%. The maximum readable turbidity was 2000 NTU.

Coatings on polystyrene were formed by spreading 0.6 g of liquid coating on the bottom (6-cm diameter) of polystyrene weighing boats (No. D50-200, LabSource, Chicago, IL) and drying at room temperature (25 °C). Coverage was reported as percentage of the bottom that was coated (three replicates); a value of less than 100% was observed when the sample beaded up before drying, leaving part of the polystyrene surface without any coating. Gloss of the dried coating on the same polystyrene surface was measured with a black cloth as background. Gloss was reported in gloss units (GU) measured at 60° from a line normal to the surface (micro-TRI-gloss, BYK-Gardner Inc., Silver Spring, MD). Gloss values were based on 3 samples, 10 gloss measurements per sample. Gloss of the uncoated polystyrene was 8.3 GU.

Coatings were applied to oranges with rubber gloves; the mean amount applied (at 20% total solids) was 0.5 g per orange (average weight, 230 g). Before application of coatings, the fruit were cleaned with a 2% solution of Fruit Cleaner 395 (FMC Corp., Lakeland, FL). Weight loss of the fruit was determined at 23 °C, 60% relative humidity (RH), 3 replicates, 5 fruit per replicate sample. The gloss of coated oranges was measured with the glossmeter previously described, here fitted with a shield having a 19-mm-diameter hole, for 10 oranges, mean of 10 readings per piece of fruit (Hagenmaier and Baker, 1995). Coating "fracture" was determined subjectively with oranges stored for 1 week at 23 °C by hitting together two pieces 3 times, rubbing them against one another in circles 10 times, and then wiping the contact surfaces with a black cloth and rating the amount of coating found on the cloth (1.0 = none; 2.0 = minimal; 3.0 = significant but acceptable; 4.0 = heavy and unacceptable; and 5.0 = virtually all coating removed). Each reported value is based on four trials.

Permeabilities to oxygen and water vapor were determined at 30 °C for coatings of approximately 3-mil (76 μm) thickness formed by drying the microemulsions on low-density polyethylene and cellulose acetate films, respectively. Oxygen permeability was measured at approximately 60% RH, with the humidity adjusted to that value by immersing the carrier gas bubbler in a 21 °C water bath. Except for this relative humidity adjustment, the oxygen permeability was measured according to ASTM D3935-81, five samples per trial, using the Ox-Tran 100 (Mocon, Minneapolis, MN). Water vapor permeability was measured according to ASTM F1249-89 with 0% RH on the uncoated side of the cellulose acetate film and 83% RH on the coated side, two samples per trial, using the Permatran W1A (Mocon). Particle size distribution of wax globules in a liquid microemulsion was determined in the equipment manufacturer's laboratory with a Nicomp 370 Submicron Particle Sizer (Particle Sizing Systems, Holland, PA). Melting points are those of the nonvolatiles, measured on samples first dried at 145 °C for 2 h. The melting point reported is the midpoint of the range determined with a visual melting point apparatus (Nalge Co., Rochester, NY).

Statistix 4.1 (Analytical Software, Tallahassee, FL) was used for computation of pooled standard errors from one-way analysis of variance, for Pearson correlations (reported as *r* values) of the various properties reported in Tables 2–4, and for stepwise linear regression (reported as *p* values) of those same properties as dependent variables against ingredients as the independent variables.

RESULTS AND DISCUSSION

Approximately 80 wax microemulsions were prepared from wax, fatty acid, water, and ammonia. Trial and

Table 2. Hach Turbidity and Percent of Solids Found in Cream

sample	turbidity (NPU)	cream (%)	sample	turbidity (NPU)	cream (%)
BW2	>2000	14	CR5	1207	0.00
BWCN2	>2000	2	CRBW2	1870	0.00
BWCN3	261	0.00	CRCN2	1717	0.00
BWCR3	>2000	5	CRPV2	>2000	0.6
CN2	917	0.00	CRPV3	622	0.00
CN3	661	0.00	PE2	278	0.00
CN4	614	0.00	PE3	368	0.00
CR2	417	0.00	PEPV2	1846	0.3
CR3	770	0.00	PEPV3	>2000	4
CR4	756	0.00	SE	45	

error was used to find which fatty acids were suited to the different waxes and also to find the minimum amount of ammonia needed. The 19 microemulsions chosen for more detailed study are representative of those made (Table 1).

Properties of the Liquid Formulations. It is generally considered that low turbidity is an advantage for wax microemulsions used as coatings (Eaton and Hughes, 1950). Preliminary observations indicated that turbidity tended to be high for ammonia-based wax microemulsions using oleic acid as the sole source of fatty acids, although that is the fatty acid generally used in morpholine-based wax microemulsion formulations. For the present work, palmitic acid and myristic acid were tried as replacement for part or all of the oleic acid (Table 1). Lauric acid proved to be a poor emulsifier, and stearic acid is known to produce opacity and irreversible blooming (Chalmers, 1971).

However, some problems were traced to using fatty acids other than oleic. Good, translucent microemulsions of polyethylene, carnauba, or candelilla wax were made that contained commercial grade palmitic acid as the only source of fatty acid. However, when these were stored for about a month at 25 °C, a solid phase, possibly crystals of fatty acid, formed. No such solids formed in beeswax microemulsions made with palmitic acid. Further, as will be discussed, formulation CR4—with Hystrene 9014 as the only source of fatty acids—did not form smooth coatings at room temperature. Finally, as the amount of saturated fatty acid increased, coatings tended to be more brittle.

High turbidity of the liquid formulation was highly correlated ($r = 0.96$) with the presence of some wax globules sufficiently large to rise to the surface as cream (Table 2). From regression analysis, turbidity was associated with inclusion in the formulation of beeswax or petroleum wax ($p < 0.0001$). However, these values of turbidity were measured without any attempt to separate the cream layer, and it is noted that beeswax emulsion BW2, which had the highest cream content, eventually (after 1 year) separated by gravity to give a lower phase with turbidity of 280 NTU at 20% total solids. Thus, by mechanical separation of cream, the preparation of clear beeswax microemulsions is possible even from the present formulations.

Globule diameter was determined for one carnauba wax emulsion that did not cream, which had turbidity at 20% total solids of 250 NTU. Volume-weighted mean globule diameter was 0.011 μm, with 99% of particles having diameter below 0.037 μm (volume-weighted, data not shown in tabular form). This low globule size suggests a mixture of microemulsion and micellar solution (Prince, 1977).

Properties of the Wax Coatings. The wax microemulsions were dried on polystyrene surfaces to form

Table 3. Properties of Wax Coatings Made by Drying Microemulsions on Polystyrene at 25 °C

sample	appearance	PS[b] coverage (%)	gloss[c] (GU)	mp (°C)
BW2	F,P,B, tacky	40	11	53
BWCN2	F,P,B	72	36	52
BWCR3	F,P,B	23	11	65
BWCN3	F,B	100	24	55
CN2	F, tacky	100	8	61
CN3	F, B	71	12	60
CN4	F	100	9	59
CR2	B,P	97	33	80
CR3	B,P	77	40	80
CR4	F, rough	92	49	78
CR5	B,P	100	45	80
CRBW2	F, B	100	39	83
CRCN2	F,B	100	20	72
CRPV2	P	12	4	68
CRPV3	P	80	81	75
PE2	P	13	NV[d]	99
PE3	P	93	63	104
PEPV2	P	12	42	85
PEPV3	B,P	10	NV[d]	76
SE		5	2	1

[a] F, flexible; P, peels off as film; B, buffable. [b] PS, polystyrene. [c] Gloss of the unbuffed coatings. The gloss of uncoated polystyrene was 8.3 GU. [d] No value. Fractured too much to measure gloss.

Table 4. Performance of Wax Coatings on Valencia Oranges

sample	wt loss (%/d)	fruit fracture rating	fruit gloss (GU)
BW2	0.18	1.2	4.9
BWCN2	0.20	1.0	6.1
BWCR3	0.23	2.8	5.7
BWCN3	0.19	1.0	5.9
CN2	0.18	1.2	5.4
CN3	0.16	1.8	6.4
CN4	0.16	1.5	5.4
CR2	0.21	5.0	6.7
CR3	0.24	4.5	7.1
CR4	0.27	4.8	6.4
CR5	0.29	4.5	6.8
CRBW2	0.23	2.2	6.4
CRCN2	0.20	2.5	6.6
CRPV2	0.28	2.2	6.2
CRPV3	0.21	3.0	7.5
PE2	0.55	2.5	6.4
PE3	0.38	5.0	6.6
PEPV2	0.29	2.8	6.9
PEPV3	0.20	2.8	5.4
uncoated fruit	1.05	1.2	4.7
SE	0.02	0.3	0.2

coatings of approximately 60 μm thickness when the coating spread over the entire surface, proportionally thicker when less surface was covered (Table 3). Stepwise regression indicated that gloss of these coatings was reduced by the presence of beeswax or candelilla wax in the formulation ($p < 0.02$). Even so, in related work we have developed candelilla wax formulations that had good gloss; these were made by using only 8 g of fatty acid/100 g of candelilla wax or by addition of protein to the formulation (Hagenmaier and Baker, 1996). Some coatings did not spread well enough to cover the polystyrene surface (Table 3). Coverage was lowest for coatings that contained petroleum wax or beeswax ($p < 0.002$). As already noted, turbidity and cream content tended to be high for petroleum wax. Coverage of the polystyrene surface also correlated negatively with turbidity ($r = 0.79$). Thus, the better the emulsification, the better the spread on a polystyrene test surface.

The wax coatings on polystyrene were buffed with a cloth and the gloss measured again (data not shown). Buffing increased the gloss for some formulations, especially those containing beeswax ($p = 0.01$), and buffing correlated positively with turbidity ($r = 0.65$). For the six beeswax-containing coatings, the gloss increased by a mean value of 14 GU upon buffing (Table 3).

The same coatings were applied to Valencia oranges (Table 4). Gloss of coated oranges was significantly higher for coatings that contained carnauba and polyethylene waxes. Gloss of the coatings on fruit and polystyrene correlated well with one another ($r = 0.80$), suggesting that evaluation of gloss on the polystyrene test surface is a useful means to estimate gloss on other surfaces—providing there is good spread and minimal cracking. Fruit gloss was negatively correlated ($r = 0.57$) with cream content of the formulations, which is as expected because large particle size is known to inhibit gloss (Bennet, 1975). Nevertheless, no statistical relationship was found between turbidity and gloss for those formulations with turbidity of <2000 NTU. Absence of cream was therefore not sufficient to ensure gloss of the coating.

Fracture of the orange coatings, measured 1 week after application, tended to be higher for those coatings

that contained carnauba wax, polyethylene wax, and/ or saturated fatty acids, based on linear regression. There was significant correlation between fracture and gloss ($r = 0.66$). Because of the unattractive appearance of coatings that flaked off, a score of >3.5 on the fracture scale would seem to disqualify a coating for use on oranges. Nevertheless, even these relatively brittle coatings may be suitable for a food that is more rigid than an orange, or subjected to less stress than used for the test, which was admittedly of considerable magnitude.

Melting points (Table 3) of the wax coatings appeared to be a useful point of reference, even though high melting points did not assure good gloss. No coatings with melting points below 72 °C had fruit gloss higher than the median value of 6.4 GU, and only one (BWCN2) had gloss on polystyrene higher that the median value of 33 GU. Unfortunately, however, only one coating with a melting point below that temperature (CRB2) exhibited a fracture score below the median value of 2.8. Thus, it is a challenge to adjust the formulation to achieve gloss without the coating becoming brittle. Treffler (1952) reported that wax molecules having melting points of 75–90 °C made the best self-polishing waxes. An advantage of using melting points is that they can be estimated from ingredient content, thus making it possible to limit the number of coatings to be tested experimentally. The measured values of melting point (Table 3) differed by an average of 5 °C from values estimated from the weighted averages of ingredient melting points (values not shown).

All of the wax coatings were effective in limiting weight loss of oranges, including those that easily fractured when dried on fruit or polystyrene and also including those that spread poorly on the polystyrene test surface (Table 4). Polyethylene wax coatings were least effective in reducing weight loss of the oranges, but even these reduced weight loss by half. Weight loss was similar with the wax coatings other than polyethylene.

Drying temperature was particularly important for CR4, which at 25 °C dried to a very rough solid with gloss of 6 GU. However, its gloss was 15 GU when dried at 30 °C, 33 GU at 35 °C, and 49 GU at 36–45 °C (data not shown). Thus, a drying temperature above 36 °C
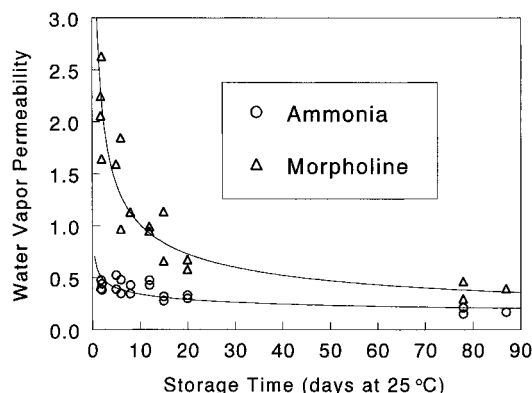
Figure 1. Water vapor permeability (g mil m^{-2} day^{-1} mmHg^{-1}) at 30 °C, 83% RH, of emulsions made with 100 g of candelilla wax, 12 g of palmitic acid, and 12 g of oleic acid, plus either ammonia or morpholine. Permeability of 1.0 g mil m^{-2} day^{-1} mmHg^{-1} is equivalent to permeance of 26.4 g m^{-2} day^{-1} through a 25.4-mm-thick film with 83% RH on one side and 0% RH on the other.

seemed necessary for this microemulsion. Coatings applied to fruit were dried at hot-air temperature of 48 °C, which may explain why oranges with CR4 had gloss comparable to that with the other formulations (Table 4).

It may be noted that CN2 was tacky (Table 3). This coating, which performed well as an orange coating (Table 4), contained 24 g of oleic acid/100 g of candelilla wax (Table 1). In a related work, the oleic acid was reduced to 20 g, which reduced the tackiness, and performance on citrus fruits was virtually the same (data not shown). In general, the formulations presented in Table 1 can be adjusted somewhat to vary properties of the coatings.

The water vapor permeability at 30 °C of candelilla wax coating CN4 after 10 days of drying time was 0.4 g mil m^{-2} day^{-1} mmHg^{-1} (Figure 1). This is virtually the same as the permeability of low-density polyethylene film, which is a relatively good barrier to water vapor compared to other packaging films (Sacharow and Griffin, 1980).

Water-vapor permeability of coating CN4 decreased with time (Figure 4). To determine why, a similar microemulsion was made with morpholine as replacement for the ammonia. Water vapor permeability of the morpholine-based coating decreased markedly during the first 3 weeks of storage. In contrast, permeability of the ammonia-based coating was lower and leveled off much sooner, presumably caused by a faster rate of evaporation of NH$_3$ compared to morpholine. Thus, use of morpholine in edible coatings presumably would result in consumption of this ingredient.

The oxygen permeabilities of the candelilla wax coatings at 25 °C after 10 days of drying time were 2350 and 6930 mL mil/(m^2 day atm), respectively, for the NH$_3$- and morpholine-containing formulations (mean values for five samples, data not shown). These values are about the same as those of low- and high-density

polyethylene, respectively, which are not good barriers to oxygen transfer (Sacharow and Griffin, 1980). Nevertheless, as recently shown, the water vapor and oxygen permeabilities of wax coatings can be considerably changed by addition of protein to the formulations (Hagenmaier and Baker, 1996).

Wax Coatings and the FDA. Food applications of wax coatings are subject to regulations on their various ingredients as promulgated by the FDA (1995). Formulations that contain polyethylene wax (Table 1) would be restricted to specified fruits, by CFR 172.260. Formulations containing beeswax or petroleum wax have limited applicability to foods because of 21 CFR 184.1973 and 172.886, respectively. The other formulations would seem to have broad approval as food or pharmaceutical coatings, in view of 21 CFR 184.1976 (candelilla wax), 21 CFR 184.1976 (carnauba wax), 21 CFR 172.860 (fatty acids), 21 CFR 184.1139 (ammonia), and 21 CFR 173.340 (polydimethylsiloxane).

LITERATURE CITED

Bennet, H. *Industrial Waxes*; Chemical Publishing: New York, 1975.

Chalmers, L. Polishes. *Paint Manuf.* **1971**, *41* (8), 30−31.

Eaton, J. L.; Hughes, F. A. Amine emulsifiers for carnauba wax emulsions. *Proc. Annu. Meet., Chem. Spec. Manuf. Assoc.* **1950**, Dec, 197−200.

FDA. *Code Fed. Regul.* **1995**, Title 21.

Hagenmaier, R. D.; Baker, R. A. Internal gases, ethanol content and gloss of citrus fruit coated with polyethylene wax, carnauba wax, shellac or resin at different application levels. *Proc. Fla. State Hortic. Soc.* **1995**, *107*, 262−265.

Hagenmaier, R. D.; Baker, R. A. Edible coatings from candelilla wax. *J. Food Sci.* **1996**, *61* (3), 562−565.

Hitz, C. W.; Haut, I. C. Effects of waxing and pre-storage treatments upon prolonging the edible and storage qualities of apples. *Bull., Agric. Exp. Stn., Univ. Md.* **1942**, No. A14, 1−44.

Morales Guerrero, J. C.; Gallardo, J. M. L. Composition of matter for the coating of plant products for their preservation and process of making same. U.S. Pat. 4021262, 1977.

Prince, L. M. Schuman's microemulsion. In *Microemulsions, Theory and Practice*; Prince, L. M., Ed.; Academic Press: New York, 1977.

Sacharow, S.; Griffin, R. C. *Principles of Food Packaging*; AVI Publishing: Westport, CT, 1980.

Treffler, A. Gloss of self-polishing wax. *Soap Sanit. Chem.* **1952**, *28* (4), 147−169.