temperature for 30 min., and tempering for 15 days at 25°C. Curve B was obtained on chilling the melted sample at 0°C., holding it at this temperature for 30 min., and putting it in the dilatometer bath held at about −38°C.

The approximately 14% of diunsaturated glycerides in cocoa butter (17) melt at temperatures below those of the two main components. According to the curves in Figure 4, melting starts at about 0°C. From Curve A, Figure 4, it was calculated (18) that this sample of cocoa butter after being well-tempered contained the following percentages of liquid:

Temperature, °C.	Content of liquid, %
0	0.6
5	1.9
10	4.1
15	6.8
20	10.8
25	16.7
30	36.1
34.1	100.0

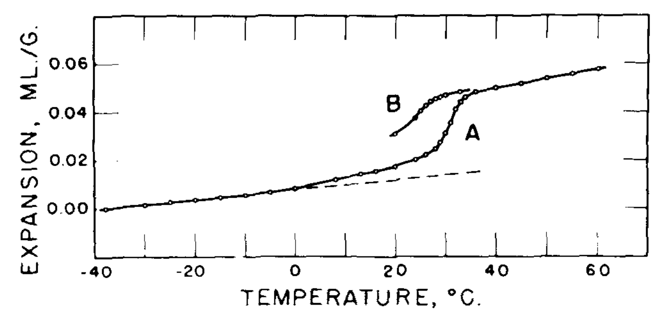

FIG. 5. Dilatometric curves for a sample of sweet milk chocolate, coating type: A, the two major glycerides of cocoa fat in Form I; B, the two major glycerides in Form II.

Dilatometric curves also were obtained for a sample of commercial, sweet milk chocolate, coating type (Figure 5). To obtain Curve A the chocolate, as received from the manufacturer, was tempered for several months at room temperature. A small block of this chocolate was then sealed in a dilatometer, and measurements were made without the usual melting, solidification, and tempering treatments in the dilatometer. To obtain Curve B a tempering procedure similar to that used to obtain Curve B for cocoa butter was employed.

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A Small Laboratory Model, Wiped-Surface Heat Exchanger for Chilling and Texturating Shortenings[1]

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A miniature Votator type, wiped-surface heat exchanger for chilling and texturating shortening has been described.

The package unit, mounted on a table about 2 x 4 ft. in dimensions, fitted with casters for mobility, needs only to be plugged into an electrical outlet for operation, operates at fat feed-rates of 10 to 80 lbs. per hour, with an integrated ¾ ton Freon refrigeration unit capable of holding the chilling unit to ±1°F. in the range −30°F. to +60°F., 4-step pulley agitator drives on both chilling and texturating units giving 330 to 1170 r.p.m. speed range, aluminum alloy chilling and texturating units, fat and air Flowrators with needle valve control, free-swinging wiper blades, and a few other minor features that lead to smooth operation.

The unit has been found useful in our laboratory to process various types of shortenings for research purposes, to supply special shortenings to prospective customers for evaluation, and to check the operation of the plant Votators.

[1] Presented at 51st Annual Meeting, American Oil Chemists' Society, Dallas, Tex., April 4–6, 1960.

IN THE MID-1930's the closed continuous internal chiller and plasticizer, known as the Votator, came into use and has substantially replaced the chill roll. Bailey (1), Dawson (2), Fincher (3), James (5), Joyner (6), McMichael (7,9), and Slaughter (9) have given excellent descriptions of the various systems used for chilling and texturating plastic fats, including margarine.

In 1957 Steffen and Vander Wal (10) described a batch procedure for plasticizing small samples of fats in the laboratory, using a refrigerated Kitchen-Aid Mixer (Model K-4-B). More recently, in 1959, Harrington, Bates, and Stingley (4) described a batch laboratory-size plasticizer, which will chill and plasticize a 1,300-g. sample in 4 min., giving a product very similar in consistency and performance to a plant plasticized product.

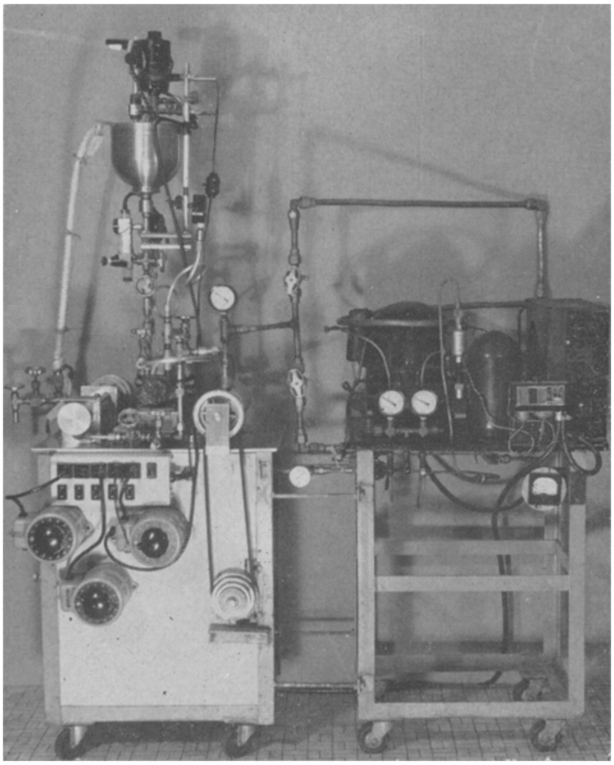

FIG. 1. Laboratory Emulsorator.

The Wesson Laboratories long needed a miniature Votator type of unit, scaled down to match the capacity of the laboratory hydrogenation and deodorization units and capable of duplicating plant Votator results on as little as 3 to 10 lbs. of shortening. Prior to the construction of this laboratory plasticizer, we used a miniature chill roll, 6 in. long by 5½ in. in diameter, which would duplicate plant plasticized samples in creaming and icing, but the package appearance was lumpy, and it was a batch operation limited to 3 to 6 lbs.

Design and Operation

The authors have recently designed a miniature Votator type of unit with a hold-up of only 1 lb. of fat (Figure 1), an output range of 10 to 100 lbs. per hour, at 20 to 200 lbs. of pressure, 4-step pulley agitator drives on both chilling and texturating units giving 330 to 1170 r.p.m. speed range, aluminum alloy welded jacket chilling unit 2 in. in diameter by 7 in. long, free-swinging wiper blades, over-size rotary gear pump with bypass needle valve throttle, fat and air Flowrators with needle valve control integrated ¾-ton Freon refrigeration unit capable of holding the chilling unit to $\pm 1°F$. in the range $-30°F$. to $+60°F$., conventional "B" unit type aluminum alloy texturating unit with variable infrared heat input, electrically heated fat return line to feed bowl, and a stainless needle valve discharge nozzle.

We have adopted the term, Emulsorator, for the lab unit, based on the fine emulsification of nitrogen or air into the fat induced by the over-sized gear pump and by-pass feeding the chilling unit.

A schematic fat flow-diagram of the Emulsorator is shown in Figure 2. In operation the melted fat from the feed bowl passes through the fat Flowrator to the over-sized rotary gear pump. The fat Flowrator is installed so that it is possible to by-pass the Flowrator by closing the fat Flowrator needle valve control and opening the stainless needle valve downstream, thus allowing the fat to pass directly into the rotary gear pump. The over-sized rotary gear pump feeds a mixture of melted shortening and air (or nitrogen) to the chilling unit under 20 to 200 lbs. of pressure. The super-chilled fat flows under pressure from the chilling unit to the texturating unit through a short section of aluminum tubing containing a dial thermometer and a stainless needle valve so that the chilling unit may be kept under higher pressure than the texturating unit. The plasticized shortening discharges from the texturating unit through a stainless needle valve. The fat feed reservoir is heated by a thermostatically controlled immersion heater so that fat feed temperature to the chilling unit may be maintained at the desired temperature.

The first chilling unit was constructed of stainless steel and was fitted with a cooling jacket and internal free-swinging blades which wiped the inner walls of the chilling unit. However, because of the superior thermo conductance of aluminum over stainless steel, we later used a special hard aluminum alloy in the construction of the chilling and texturating units for the high rate of heat transfer.

Micarta or aluminum alloy free-swinging blades for positive wiping and puddling of the shortening in the chilling unit eliminates undesirable metal contamination. Aluminum tubing instead of pipe lines are used for most connections for flexibility and ease of take-down. Fat and air (or nitrogen) feed-rates are accurately controlled by sensitive Flowrator type of Rotameters, and dial thermometers or thermocouples at all critical points are used for temperature control.

The Freon jacket around the chilling unit has two outlets, one at each end of the jacket with a valve on the Freon outlet near the discharge end of the chilling unit. This set-up makes it possible to throw most of

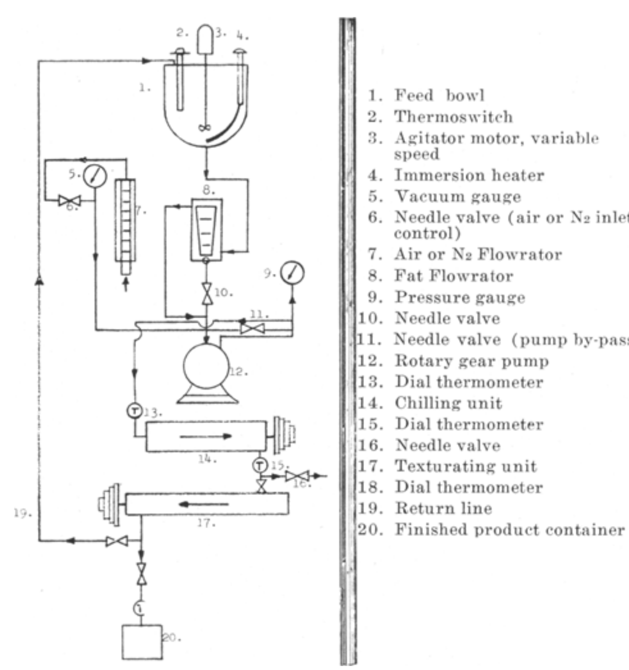

FIG. 2. Schematic flow diagram of the Emulsorator.

TABLE I

The Effects of Emulsorator Conditions on the Quality of Various Types of Shortenings

	Emulsorator conditions								Quality tests on package samples			
Sample No.	Output (lbs./hr.)	Chilling unit jacket temp. (°F.)	Temp. product from chilling unit (°F.)	Temp. product from texturating unit (°F.)	Back pressure on chilling and texturating units (p.s.i.g.)	Temp. fat to chilling unit (°F.)	Agitator speeds (r.p.m.) Chilling unit	Agitator speeds (r.p.m.) Texturating unit	Icing test (specific gravity at 30 min.)	Consistency (Scoco needle penetration) 60°F.	Consistency (Scoco needle penetration) 90°F.	Whiteness (MgO = 100)
S-1(a)	8,100	−8	64	86	250	110	400	90	0.49	73	147	90
S-10	62	30	58	75	40	126	510	1170	0.51	67	132	90
S-17	45	30	55	73	50	124	330	770	0.49	70	138	90
S-23	45	20	55	76	45	125	1150	770	0.50	72	140	88
S-27	59	10	60	74	45	127	1150	770	0.49	69	129	87
Q-1(b)	6,000	−1	68	86	250	112	400	90	0.58	56	147	93
Q-2	59	40	64	76	30	126	750	1170	0.57	65	130	91
Q-9	31	40	56	76	25	122	510	770	0.59	75	149	90
Q-18	62	20	55	70	54	127	510	770	0.57	64	127	90
Q-24	45	30	52	74	41	124	510	1170	0.58	71	134	92
QO-1(c)	8,600	6	66	90	250	112	400	90	0.76	52	103	93
QO-2	28	40	61	87	45	120	750	1170	0.74	52	98	91
QO-9	28	20	64	89	65	124	1150	1170	0.69	52	101	92
QO-12	40	30	60	85	130	126	510	1170	0.74	50	90	93
QO-14	29	20	54	87	145	126	510	1170	0.72	50	97	91

[a] Plant plasticized, retail, household emulsifier type of vegetable shortening, control on "S" series.
[b] Plant plasticized, emulsifier type of baker's vegetable shortening, control on "Q" series.
[c] Plant plasticized, emulsifier type of baker's meat-fat shortening, control on "QO" series.

the refrigeration to the feed end of the chilling unit, thereby allowing a slight warming of the fat as it passes through the discharge end. This warming, puddling, and tempering in part of the chilling unit makes it function as a texturating unit and serves to increase the texturating unit capacity when it is desired to puddle the shortening. The Emulsorator refrigeration unit has been fitted with a unique combination of heat exchanger, by-pass, and hand-operated expansion valve that permits rapid and precise chilling-jacket temperature control.

The package unit, including refrigeration and all accessories, is mounted on a table about 2 x 4 ft. in dimensions fitted with casters for mobility and only needs to be plugged into an electrical outlet for operation.

Results and Discussion

The unit has been found useful in our laboratory to process 5- to 10-lb. formulations of laboratory hydrogenated and deodorized special shortenings, to study the effects of hydrogenation conditions, changes in base stock formulations, changes in emulsifiers or other minor constituents, predicting optimum plant Votator conditions, and to process 5- to 100-lb. samples of special shortenings to supply prospective customers for evaluation. We have made up to 25 six-pound runs in an 8-hr. day since a 6-lb. sample can be run in about 15 min.

A sample data sheet shown in Figure 3 lists the main operating conditions and quality tests on the Emulsorator samples, as follows: laboratory sample number, type of shortening, date, fat feed-rate, output (lbs./hr.), weight of sample, air feed-rate, c.c. air per minute, temperature of chilling unit jacket, temperature of Freon suction, temperature of fat at fat Flowrator, temperature fat to chilling unit, temperature fat from chilling unit, temperature fat from texturating unit to package, temperature rise in package, specific gravity of shortening, pressure on chilling and texturating units, pump suction, agitator speed of chilling and texturating units, and ammeter readings on the chilling and texturating units and Freon compressor.

The data sheet also shows the following quality tests on the package sample: consistency at 60° and 90°F., whiteness, icing test, creaming test, cake score, and remarks such as composition, appearance, and body of the shortening.

Table I shows the plant Votator and Emulsorator conditions used and quality tests on a retail, household emulsifier type of vegetable shortening ("S" series), an emulsifier type of baker's vegetable shortening ("Q" series), and an emulsifier type of baker's meat-fat shortening ("QO" series). The consistency

LABORATORY EMULSORATOR

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Lab. sample No.—S-17 Type shortening—Snowdrift

Fat feed-rate, meter units—0.26 lbs./hr.—45.0 wtg. sple. lbs.—3.0

Air feed-rate, meter units—7.0 cc./min.—50.0

Temp. Freon to chilling unit jacket, °F.—30 Temp. Freon suction, °F.—12

Temp. fat at fat Flowmeter, °F.—130 Temp. fat to chilling unit, °F.—124

Temp. fat from chilling unit, °F.—55 Temp. fat from texturating unit to package, °F.—73

Temp. rise in package, °F.—0 Sp. gr., package—0.81

Pressure, p.s.i.g., chilling unit—50 Texturating unit—50 Pump suction, in vac.—8

Agitator, r.p.m., chilling unit—330 Texturating unit—770

Ammeter readings—
Chilling and texturating units load amps.—6.5
Freon compressor, load amps.—5.8

Quality tests on package sample—

Age, days at °F.—2, 75–80 Consistency, Scoco needle penetration, 60°F.—70 90°F.—138

Whiteness (MgO = 100)—90

Icing test: Sp. gr. @ 30 min.—0.49 Body—good Texture—slightly curdled

Creaming test: Dry vol.— Wet vol.— %H_2O

Cake score: Pound— White layer—100 Prepared mix—

Remarks: excellent appearance and body

FIG. 3. Sample data sheet.

of the plant plasticized and Emulsorator plasticized samples was determined by the Scoco needle penetration method as described by Royce and Haskell (8). The consistency and over-all shortening quality of the Emulsorator plasticized samples are quite comparable to the plant plasticized samples.

Referring to Table 1, Sample S-17, a retail, household emulsifier type of vegetable shortening was Emulsorator-plasticized at an output of 45 lbs. per hour, with a 30°F. chilling unit jacket; temperature of the shortening from the chilling and texturating units was 55° and 73°F., respectively, and chilling and texturating unit agitator speeds were 330 and 770 r.p.m., respectively. This sample had an icing specific gravity at 30 min. of 0.49, which is equal to plant plasticized control sample S-1, a plastic range superior to the control and whiteness equal to the control. Sample Q-2, an emulsifier type of baker's vegetable shortening, was Emulsorator-plasticized at an output of 59 lbs. per hour, with a 40°F. chilling unit jacket; temperature of the shortening from the chilling and texturating units was 64° and 76°F., respectively; and chilling and texturating unit agitator speeds were 750 and 1170 r.p.m., respectively. This sample had an icing specific gravity at 30 min. of 0.57, which is slightly better than the plant plasticized control sample Q-1, a plastic range better than the control, and slightly inferior whiteness.

Sample QO-9, an emulsifier type of baker's meat fat shortening, was Emulsorator-plasticized at an output of 28 lbs. per hour, with a 20°F. chilling unit jacket; temperature of the shortening from the chilling and texturating units was 64° and 89°F., respectively; and chilling and texturating unit agitator speeds were 1150 and 1170 r.p.m., respectively. This sample had an icing specific gravity at 30 min. of 0.69, which is considerably better than the plant plasticized control sample QO-1, and a plastic range and whiteness comparable to the control.

The Emulsorator has also been used for plasticizing various fat bases containing a relatively high percentage of liquid vegetable oils.

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The Catalyzed Condensation of Phenol with Stearone and Methyl Heptadecyl Ketone[1]

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The condensation of phenol with stearone and methylheptadecyl ketone has been studied. The bisphenols and other products thus produced were identified by hydroxyl equivalent, molecular weight, infrared spectra, elemental analysis, and preparation of characteristic derivatives.

The commercial potential of this family of fatty derivatives was examined briefly from two approaches. Polymerization with formaldehyde, epichlorohydrin, and phosgene was investigated, and several fluids were prepared and screened as potential high-temperature lubricants.

OUR WORK (1) on the utilization of inedible animal fats as intermediates for commercially valuable materials suggested that bis-(hydroxyphenyl)alkanes derived from the condensation of phenol with ketones from C_{16} and C_{18} fatty acids would be worthy of investigation. Compounds of this type which are commonly referred to as bisphenols find use (2) as antioxidants, germicidal, bactericidal or teniacidal agents, pharmaceuticals, surface-active agents, fungicides, pesticides, and for the preparation of resins. They can be reacted with formaldehyde to give phenolic-formaldehyde resins (2); epichlorohydrin and caustic (2) to give polyepoxide resins; and phosgene or carbonate ester (3,5) to give a heat-resistant, dimensionally stable, thermoplastic polycarbonate.

Large-molecular-weight ketones have been prepared from saturated fatty acids and are commercially available. The use of dialkyl ketones in the preparation of bis-(hydroxyphenyl)alkanes from phenol has been reported by many investigators. They have not employed ketones of such high molecular weight as those derived from fats.

Liebnitz and Nauman (4) have reviewed much of the early patent literature and have given details as to the best procedures for the reaction of the lower dialkyl ketones with phenol. In general, our results agree quite well with their findings. They are:

1. Low temperatures, 25°–60°C., are more desirable and result in higher yields of the bisphenols than when temperatures in excess of 100°C. are used.
2. Sulfur and ionizable sulfur compounds containing a sulfur atom of apparent valence not greater than two promote the condensation of phenol with ketones. Anhydrous hydrogen sulfide was very satisfactory and has been the only sulfur catalyst employed by us.
3. Various acid-acting condensing agents, such as hydrochloric acid or a salt giving hydrochloric acid when reacted with water, are the most widely used. We have found that anhydrous hydrogen bromide or mixtures of anhydrous hydrogen bromide and anhydrous hydrogen chloride work very satisfactorily.

The ratio of reactant phenol to ketone can be varied; however when the ketones are solids, it has been advisable to use a large excess of phenol in order to maintain a liquid reaction mixture at low temperatures. Yet, even under the most favorable reaction conditions known, such reactions to produce

[1] Presented at the 51st annual spring meeting, American Oil Chemists' Society, Dallas, Tex., April 4–6, 1960.