

## Wool Wax Emulsions

By H. I. SILVERMAN

Emulsions prepared with a wool wax isolate and its ethoxylated derivative have been formulated and studied. Rheological patterns were determined over a 12-month period and flow types characterized. Globular sizes were also determined and correlated with the observed stabilities (creaming rates) and emulgent concentrations. The inapplicability of Stokes' law in theoretical calculations of creaming rate has been shown. A stable emulsion may be produced by selecting as an emulsifying agent a material that will not form a true solution with either of the emulsion phases while exhibiting an affinity for or a greater solubility (colloidal sol) in the external phase.

WOOL WAX, its numerous fractions and synthetic derivatives, enjoy wide and varied applications in the cosmetic, pharmaceutical, chemical, and other fields. The chemical composition of this natural wax is varied and extremely complex. Briefly, it may be described as a mixture of a majority of straight chain and steroid waxy esters plus a minority of free fatty acids and alcohols. A comprehensive literature survey has been recently published (1, 2) which contains, in addition to references on chemistry, numerous sources of wool wax derivatives, both the purified fractions and chemically altered components of these fractions.

It is the purpose of this paper to report on the feasibility of using two of the aforementioned derivatives as emulgents. No single component of wool wax is seemingly responsible for its ability to act as an efficient w/o emulsifier. Rather, its value as an emulsifying agent is probably due to both the alcoholic and free fatty acid components (3,4).

Wool wax components may be chemically modified to increase their dipole moment by ethoxylation (5, 6). Polarity will increase in a linear proportion corresponding to the length of the coupled ethylene oxide polymer. This hydrophilic polymer, upon reaching a definite number of ethenoxy groups per molecule will allow the preparation of a water "soluble" colloidal sol from the originally water insoluble component. Due to the high molecular weight hydrocarbon components, true aqueous solutions are not possible although transparent dispersions can be produced. In addition, the increased

hydrophilic property will tend to reverse the original emulsifying ability from w/o to o/w.

### MATERIALS

For this study an isolation product of wool wax and its ethoxylated derivative were selected as emulsifying agents. The isolation product was Lanfrax,<sup>1</sup> a water insoluble fraction, appearing physically as a stiff semisolid plastic material when at room temperature. This fraction is composed of a mixture of the higher melting range (49–51°) hard wax esters which have been removed from the lower melting components by a fractional solvent crystallization process (7).

Lanfrax WS55,<sup>1</sup> the ethoxylated derivative of the above-mentioned wax, is a nonionic surface-active and hydrophilic hard waxy material. Clear transparent colloidal sols may be prepared in water.

The balance of the emulsion systems was composed of distilled water, liquid petrolatum (viscosity 60 cps., sp. gr. 0.86), and a phenolic salt—sodium *o*-phenyl phenol<sup>2</sup> which functioned as a preservative.

### EXPERIMENTAL

**Formulations and Physical Data.**—Lanfrax was used as the w/o emulsifying agent. At room temperature in mineral oil, clear colloidal sols may be produced using up to a 1% concentration by weight with uniform but cloudy dispersions possible at greater concentrations.

Lanfrax WS55 was used as the o/w emulsifying agent. Transparent colloidal sols in water may be produced at room temperature. The Tyndall cone phenomenon was observed with aqueous solutions of this ethoxylated wax derivative.

Experimental emulsions were similarly prepared by heating the external phase of each formulation to 65–70° and dissolving the emulsifying agent in it. The internal phases were likewise heated to the same temperature. The preservative was dissolved in each of the respective aqueous phases prior to emulsification. Emulsification was then carried

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<sup>1</sup> Malmstrom Chemical Corp.

<sup>2</sup> Dow Chemical Co. (Dowicide A).

TABLE I.—FORMULATIONS

	Emulsion Number		
	02161A 100 Gm.	02161B 100 Gm.	02161C 100 Gm.
o/w Series			
1. Lanfrax WS55	3.0	5.0	8.0
2. Liq. petrolatum (visc. 60 cps.)	48.5	47.5	46.0
3. Distilled water	48.5	47.5	46.0
4. Preserve with sodium <i>o</i> -phenyl phenol <sup>a</sup> to give a final concn. in emulsion of 0.25% by weight.			
Relative consistency noted at time of manufacture.	"Thin Lotion"	"Medium Lotion"	"Heavy Lotion"
	Emulsion Number		
	02171A/1 100 Gm.	02171B/1 100 Gm.	02171C/1 100 Gm.
w/o Series			
1. Lanfrax	3.0	5.0	8.0
2. Liq. petrolatum (visc. 60 cps.)	48.5	47.5	46.0
3. Distilled water	48.5	47.5	46.0
4. Preserve with sodium <i>o</i> -phenyl phenol <sup>a</sup> to give a final concn. in emulsion of 0.25% by weight.			
Relative consistency noted at time of manufacture.	"Medium Lotion"	"Heavy Lotion"	"Very Heavy Lotion"

<sup>a</sup> Dowicide A.

out by placing the external phase, containing the emulsifying agent, in a Waring Blender connected to a powerstat (set to a dial reading of 75) and slowly adding the internal phase. After mixing 2-3 minutes, the emulsion, (which formed immediately in each case) was removed from the blender, allowed to cool to approximately 60°, and then passed twice through a piston homogenizer. Several batches of the respective emulsions (500 Gm. each) were processed by this method and were used in studying both stability and rheological patterns.

Formulations are set forth in Table I, and as can be noted each of the emulsion types was prepared at emulgent concentration of 3, 5, and 8%, respectively, by weight.

**Stability Studies.**—A 100-ml. quantity of each formulation was poured into separate matched glass cylinders of 2.5 cm. i.d. Emulsion height in these tubes was 20.5 cm. Apparent viscosities of the external emulsion phases, each of which contained the listed content of emulsifying agent, was determined at minimum shear by a Brookfield Viscometer,

TABLE II.—VISCOSITY AND SPECIFIC GRAVITY DATA DETERMINED AT 25°C.

External <sup>a</sup> Phase	Viscosity <sup>b</sup> at Minimum Shear, cps.	Specific Gravity
o/w Series		
02161A	10	1.01
02161B	20	1.01
02161C	300	1.02
w/o Series		
02171A/1	100	0.863
02171B/1	800	0.864
02171C/1	5,000	0.866

<sup>a</sup> External phase containing Lanfrax WS55 in o/w series and Lanfrax in w/o series. <sup>b</sup> Brookfield Viscometer, model LVT.

model LVT, and recorded in Table II. Specific gravities of the above-described phases were determined by the pycnometer method at 25° and are likewise recorded in Table II. At predetermined intervals emulsions were microscopically examined in order to record the globular size of the dispersed

TABLE III.—AVERAGE GLOBULAR DIAMETER AND RELATIVE DISTRIBUTION

	Days After Manufacture		
	5	30	60
o/w Series			
02161A	2-14 $\mu$ , wide variation in globular size 6 $\mu$ av.	3-15 $\mu$ , wide variation in globular size 6 $\mu$ av.	6 $\mu$ av., moderate packing of globules
02161B	2-3 $\mu$ , globules are fairly uniform	1.5 to 3 $\mu$ , globules fairly uniform and tightly packed	2 $\mu$ av., globules are uniform and tightly packed
02161C	0.4-0.5 $\mu$ , globules are uniform	0.5 $\mu$ , globules both uniform and tightly packed	0.3-0.5 $\mu$ (av. 0.5 $\mu$ ), globules are uniform and tightly packed
w/o Series			
02171A/1	2-4 $\mu$ , with variation in globular size	1.5-6 $\mu$ , with variation in globular size	1.5-7 $\mu$ (av. 3 $\mu$ ), globules not uniform and loosely packed
02171B/1	1-6 $\mu$ , with variation in globular size	1-6 $\mu$ , with variation in globular size	1-6 $\mu$ (av. 2 $\mu$ ), globules not uniform and loosely packed
02171C/1	1.5-3 $\mu$ , globules are uniform	1-3 $\mu$ , globules are uniform and tightly packed	1-3 $\mu$ (av. 1.5 $\mu$ ), globules are uniform and tightly packed

TABLE IV.—CREAMING<sup>a</sup> AND PHASE<sup>b</sup> SEPARATION, OBSERVED<sup>c</sup> AND THEORETICAL

Formula	Time, Days									
	5		10		25		60		120	
	Actual	Calcd.-C	Actual	Calcd.-C	Actual	Calcd.-C	Actual	Calcd.-C	Actual	Calcd.-C
02161A	1.5-LC	12.7	2.8-LC	25.4	4.4-LC	63.5	4.8-LC	152.4	4.8-LC	4.8-LC
02161B	0.1-LC	0.709	0.6-LC	1.42	1.0-LC	3.54	1.2-LC	8.50	1.8-LC	
02161C	0	0.003	0	0.006	0	0.016	0	0.038	0	
02171A/1	0.05-UP	0.030	0.05-UP	0.059	0.2-UP	0.148	1.1-UP	0.356	2.8-UP	
02171B/1	0	0.016	0	0.033	0	0.082	0.05-UP	0.198	0.90-UP	
02171C/1	0	0.001	0	0.003	0	0.007	0	0.016	0	

<sup>a</sup> In cm. of zone height of separated emulsion containing a lesser concentration of dispersed phase; column part-L is bottom, U is top; C is creaming. <sup>b</sup> In cm. of zone height; column part-L is bottom, U is top; P is phase. <sup>c</sup> 100 ml. of each emulsion placed into glass tubes of 2.5 cm. i.d., height of emulsion in tubes was 20.5 cm.

phase. Droplet size may be used as an aid both in stability prediction (8) and creaming rate calculations by the use of Stokes' law.

With the use of outlined techniques as a guide (9, 10), diameters of the dispersed particles were determined and then recorded in Table III. A Levy Hemacytometer with Fuchs-Rosenthal ruling and a calibrated ocular micrometer disk were employed for the counting procedure. Approximately 1000 globules in each emulsion were microscopically measured. Brownian movement was noted in each of the experimental emulsions and was especially significant in the w/o series.

Creaming and phase separation were noted by measuring and recording their respective zone heights at definite intervals. These measurements coincided with times of globular examination.

Observations on the former two phenomena were recorded over a period of 4 months (Table IV). Separation zone placement in the stability columns is also recorded.

**Creaming Rate Calculation.**—Certain of the aforementioned data (diameter of dispersed globule, viscosity, and specific gravity) may be used in theoretical calculations of the creaming rate by applying Stokes' law. The actual zone distance through which the dispersed globules moved during the stability observation has been compared to the theoretical distance of movement calculated by Stokes' law (Table IV). As an example of a theoretical calculation the rate of globule movement (creaming) is herewith calculated for emulsion 02161A for a 5-day period of standing.

1. Viscosity at minimum shear of external phase containing emulsifying agent. . . . . 0.1 poise
2. Specific gravity of external phase containing emulsifying agent. . . . . 1.01
3. Specific gravity of the dispersed phase (liquid petrolatum). . . . . 0.86

$$\text{Stokes' eq.: } V = \frac{d^2(P_1 - P_2)g}{18 \eta}$$

where  $V$  = velocity of sedimentation;  $d$  = diameter of globules of the dispersed phase;  $P_1$  = specific gravity of the dispersed phase;  $P_2$  = specific gravity of the dispersion medium;  $g$  = gravitational constant;  $\eta$  = viscosity of the dispersion medium.

Solving for  $V$

$$V = \frac{(6 \times 10^{-4})^2 (0.86 \times 1.01) 980}{18 \times 0.1} = 2.94 \times 10^{-5} \text{ cm./sec.}$$

To determine the rate of globular rise in a 5-day period, then multiply by a factor of  $4.32 \times 10^5$ . Since there are 60 seconds in a minute  $\times$  60 minutes in an hour = 3600 seconds. In 24 hours there are 86,000 seconds and in 5 days there would be 432,000 seconds:  $(2.94 \times 10^{-5}) \times (4.32 \times 10^5) = 12.70$  cm./5-day rate of globule rise since the density of the dispersed phase is less than that of the continuous phase.

With the exception of theoretical calculations at the 120-day period, both actual and calculated zones have been recorded (Table IV).

TABLE V.—APPARENT VISCOSITIES O/W SERIES<sup>a</sup>

Emulsion age Formula	Viscosity, cps.			
	5 Days	30 Days	60 Days	12 Mo.
02161A				
Speed, r.p.m. (Spindle no. 2)	60	75	73	70
	30	95	90	85
	12	148	138	125
	6	210	200	175
	3	330	300	280
	1.5	500	400	360
02161B				
Speed, r.p.m. (Spindle no. 2)	60	320	308	287
	30	460	440	410
	12	790	775	725
	6	1265	1220	1170
	3	2060	2050	1950
	1.5	3480	3480	3240
02161C				
Speed, r.p.m. (Spindle no. 3)	60	1930	1750	1600
	30	2948	2700	2500
	12	5500	5000	4650
	6	8900	8200	7800
	3	14,920	14,000	13,200
	1.5	25,280	24,400	23,200

<sup>a</sup> Brookfield Viscometer, model LVT, room temperature 23-25°C.

TABLE VI.—APPARENT VISCOSITIES W/O SERIES<sup>a</sup>

Emulsion age Formula	Viscosity, cps.			
	5 Days	30 Days	60 Days	12 Mo.
02171A/1				
Speed, r.p.m. (Spindle no. 3)	60	830	780	570
	30	1056	1000	700
	12	1550	1450	900
	6	2300	2100	1300
	3	3600	3200	1800
	1.5	5600	5600	3040
02171B/1				
Speed, r.p.m. (Spindle no. 4)	60	5300	3700	2350
	30	7600	5600	3260
	12	13,000	9500	5400
	6	22,000	15,000	8500
	3	35,400	26,000	14,400
	1.5	58,000	46,000	25,200
02171C/1				
Speed, r.p.m. (Spindle no. 4)	60	8950	4700	3500
	30	15,400	14,200	6800
	12	27,500	26,000	11,500
	6	47,000	45,000	19,500
	3	84,000	80,000	35,000
	1.5	140,000	144,000	64,000

<sup>a</sup> Brookfield Viscometer, model LVT, room temperature 23-25°C.

**Apparent Emulsion Viscosities.**—Emulsions were stored in 500-ml. quantities in suitable containers which were inverted three times prior to instrumental analysis of viscosities. In addition, at 3-day intervals for a 2-month period only, containers were opened, closed, and shaken vigorously. As was expected, all of the emulsions behaved similarly when their flow properties were studied. All were non-Newtonian and exhibited plastic flow. Apparent viscosities at time intervals have been recorded in Tables V and VI. Corresponding to these tables and using a semilog scale, Fig. 1 plots viscosity characteristics of the emulsions when they are subjected to increasing shearing rates. Finally, Figs. 2 and 3 illustrate a pseudoplastic type of non-Newtonian flow for all of the emulsions as well as an apparent yield value. The latter may be easily extrapolated from the base of each of the flow curves. Shearing rate was recorded as r.p.m. and shearing stress (torque) as scale readings of the Brookfield Viscometer, model LVT. It is most important when studying rheological characteristics of a non-Newtonian system to record all variables. In this experiment, temperature, emulsion age, Brookfield spindle size, rate and shear, and shearing stress or torque (Brookfield scale readings) have been recorded in order to classify properly rheological behavior.

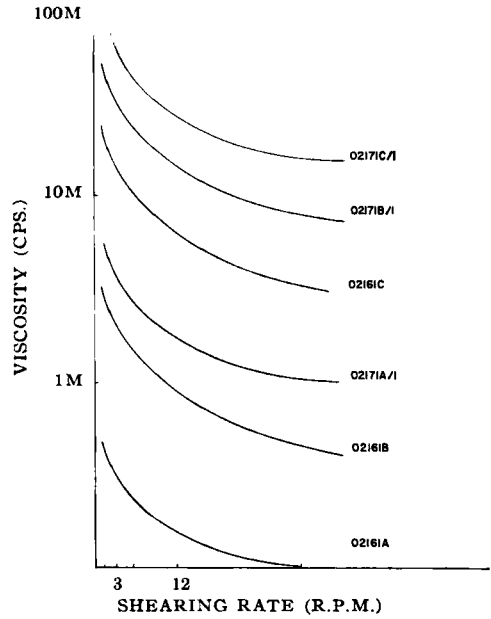


Fig. 1.—Rheogram characterizing type of flow. Sample age 5 days.

**DISCUSSION AND CONCLUSIONS**

In general, over the time period during which data

were collected and recorded in this study (12 months), all emulsions of both types were stable in

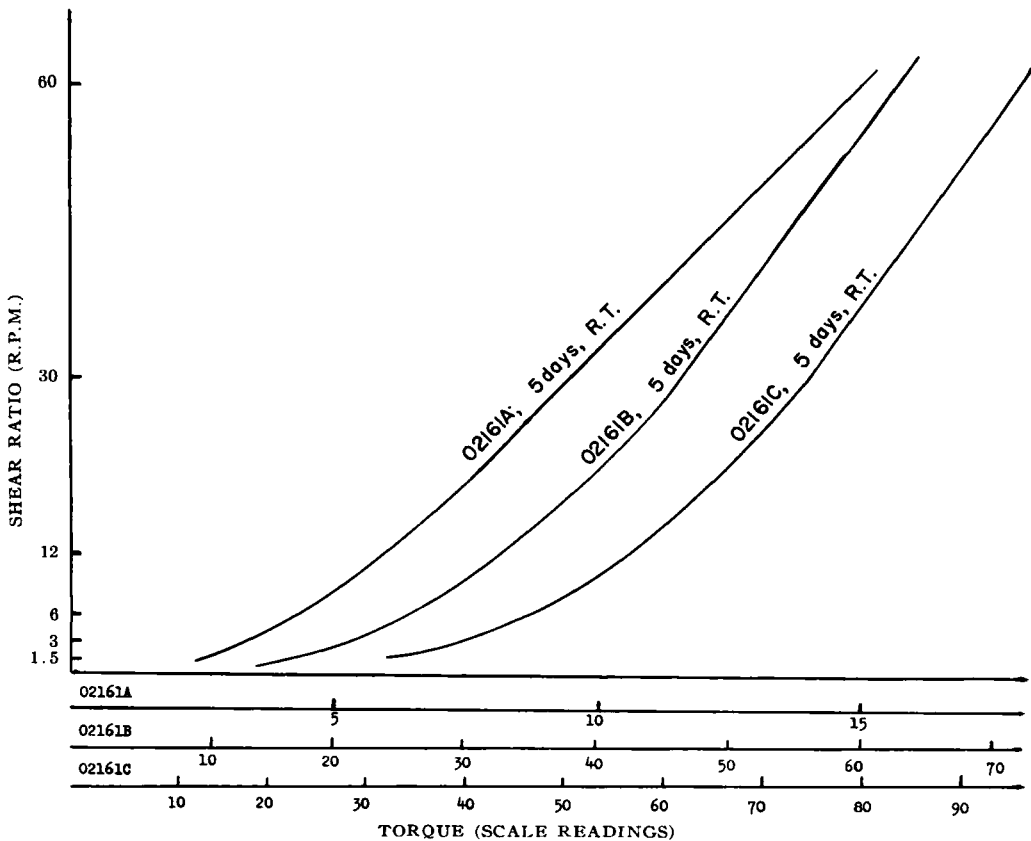


Fig. 2.—Rheogram illustrating type of flow. Shearing Rate (r.p.m.) vs. Torque (Scale Readings).

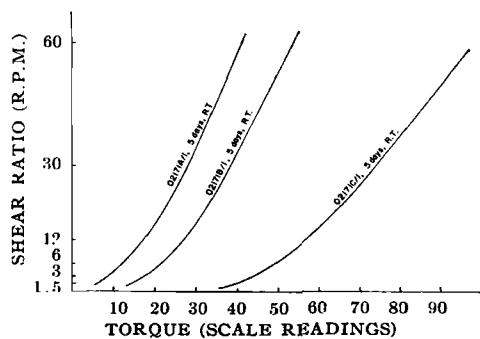


Fig. 3.—Rheogram illustrating type of flow. Shear Rate (r.p.m.) vs. Torque (Scale Readings).

regard to cracking. In the o/w series some creaming occurred when the concentration of emulsifying agent (Lanfrax WS55) was held at 3 and 5%, respectively.

As would be expected with the moderate creaming exhibited, simple container inversion was sufficient to reblend these formulas. At an 8% concentration a uniformly stable product resulted with good stability (both observed and when theoretically calculated by a commonly accepted procedure). The latter emulsions' optimum stability is interesting in light of common practice to use thickening agents and emulsifier blends to stabilize emulsion systems. Good stability was observed in all of the w/o emulsions, with again optimum stability at the higher emulsifier concentrations. The greater viscosity of the external phase in this series assisted in stabilization. It is interesting to note that Lanfrax as a w/o emulsifying agent exhibits dual functions of thickener as well as emulsifier.

All of the rheograms show expected patterns. Flow may be characterized as pseudoplastic with yield values.

It is interesting to note that the o/w series exhibited a less changeable viscosity pattern than the w/o group. Viscosity drop was generally progressive for the first 2 months, and leveling off afterward. The repeated shaking during the initial 60 days may have contributed further to a weakening in gel pattern. Finally, the omission of an antioxidant from the w/o series and a possible interaction between the phenolic preservative and wax esters could also have played some part in the change of rheological characteristics.

Globular size was generally unchanged over the 2-month observation period. As the degree of creaming (when it occurred) was only moderate, this is not unexpected.

Contrary to Becher (8), Brownian movement was readily noted in all emulsions and this phenomenon was most apparent in the w/o series. That the w/o emulsions were, in general, somewhat less uniform in globular size may be a contributing factor. At the same time, however, the varied droplet size should also tend to increase stability by

improved packing. Evidence of this assumption may be noted by examining data in Tables II and III. Observable instability proceeded at a lower rate in the w/o series than in the o/w emulsions.

While a higher viscosity of an emulsion external phase will improve shelf life through retardation of the creaming rate, such improvement in stability is necessarily coupled with globular packing.

The occasional application of Stokes' law to emulsion systems would appear to have several faults. To apply this law (which is suitable for highly dilute (under 0.5%) suspensions) to emulsion systems is seemingly in error. Few of the calculated rates of globular rise correspond to the observed rate. In addition, the following important considerations are neglected: globular size variation; dispersed phase charge (zeta potential); tendency of globules to coalesce; free globular movement hindered due to close packing; Brownian movement affecting globules of  $1\ \mu$  and less diameter; temperature; concentration of emulsifying agent; and viscosity of dispersed phase may be non-Newtonian.

Stokes' law, in respect to emulsions, should be reserved simply to aid in determining the direction of creaming. It is obvious that a perfectly stable emulsion is one which does not exhibit creaming and/or phase separation. Of course the final stage of instability is where the system eventually reverts to completely separate phases (thermodynamically stable state). Since an emulsion is a potentially changeable system, its natural tendency is toward reversion. Reversion may be delayed through:

- A Use of suitable equipment to produce dispersed globules with diameters of  $1 \pm 0.5\ \mu$ ;
- B Maintaining the specific gravity of the emulsified phases as close together as possible; and
- C Use of an emulsifier to form a suitable interfacial film (which functions to prevent globular coalescence) as well as to cause an increase in the viscosity of the external phase.

This film may be produced by an agent having a greater solubility (colloidal sol) in one phase than another but yet will not form a true solution in either one.

Other factors such as temperature, viscosity, and phase volume ratio, play a part; however, the aforementioned points are those of greatest significance in emulsion stabilization.

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