that formed by a hexane solution of pure dianilinogossypol under similar conditions.

Reagent blanks included with 14 sets of determinations by the proposed method gave an average density of 0.0015 on the Beckman DU spectrophotometer. The O.D. range was −0.002 to 0.004. These values are sufficiently low that it is not necessary to run reagent blanks with each set of determinations.

Samples of 0.5000 g. of meals Nos. 7 to 12 were treated with 2 ml. of alcohol, extracted with chloroform, and diluted as directed, then read on the Beckman DU spectrophotometer. The mean O.D. was 0.0047 with a range of 0.003 to 0.007. These low values are the justification for using chloroform as the reference solution. The extract may be used as a reference solution to correct for the low O.D. obtained from the chloroform extract when the ultimate in accuracy is required.

There were no significant differences in the results obtained with the Beckman DU spectrophotometer and the Evelyn colorimeter on meals Nos. 7 to 12 by the proposed method, Table III. These data indicate that instruments such as the Evelyn colorimeter give accurate results by this method, and any good photoelectric colorimeter or spectrophotometer should give satisfactory results after establishing a calibration curve.

Along with simplicity, greater accuracy, and a high degree of precision the proposed method offers the advantage of a greatly reduced time requirement as compared to methods previously used. An analysis may be completed in about 1.5 hrs.

Summary

An improved method has been developed for the determination of total gossypol in cottonseed and cottonseed meal. The sample is heated with aniline to convert the gossypol to dianilinogossypol, which is extracted with chloroform and measured spectrophotometrically. The values for total gossypol are slightly higher and more accurate and precise as determined by the proposed method because of more complete extraction than by a recent p-anisidine method or the revised A.O.C.S. Tentative Method Ba 8-55. The advantages of the proposed method are its simplicity, accuracy, reproducibility, and expeditiousness.

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Fat Emulsions. Effect of Polyoxyethylene and Alkyl Content of Emulsifiers on Stability to Sterilization[1,2]

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IN DISCUSSIONS of the theoretical and practical aspects of emulsions as found in the extensive literature of the subject, for example, the book by Berkman and Egloff (1), the role of the specific influence of emulsifying agents on certain properties of systems of oil (vegetable or hydrocarbon) and an aqueous phase in constant proportion has received little attention. Sherman (2) reports the influence of the emulsifying agent on the viscosity of water-oil emulsions at room temperature, stating that he found but few previous observations on the specific influence of emulsifiers. Broughton and Squires (3) report a similar study with oil-water systems, in which the effect of the type of stabilizer on the viscosity was determined. These two reports, concerned with tests made at room temperature, constitute the only available information as to the effect of various emulsifiers on the properties of emulsions.

In the development of fat emulsions for intravenous alimentation, one requirement is that such emulsions must be stable under conditions required for sterilization, namely 121°C. for 10–30 min. In the literature reports cited above, no reference is made to the characteristics of fat emulsions at elevated temperatures. Heat, in fact, is a means of demulsification in a standard test for emulsion stability (4). Differences in the characteristics of emulsions at ordinary temperatures and at 121°C. therefore are to be expected and actually were found. These differences most probably are caused by variations in interfacial tension, solubility, or other phenomena involving the emulsifying agents. Emulsifiers of the nonionic type are soluble in water because of association of their hydrophilic groups with the water molecules. As the temperature of such solutions increases, the degree of association decreases until at a critical temperature the point of solubility inversion is reached and turbidity follows. Benerito and Singleton (5), in determining the effect of heat on the solubility of hydrophilic emulsifiers, found that the critical temperature at the point of solubility inversion of nonionic emulsifiers in water is highest for those emulsifiers which are very hydrophilic. As the content of hydrophilic polyoxyethylene groups in

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nonionic emulsifiers increases, the temperature at which solubility inversion occurs also increases.

Emulsification at present is more or less empirical in nature in that no basis exists whereby the weight percentage of emulsifier needed to impart certain characteristics to oil-in-water emulsions can be calculated. Griffin (6) has developed the HLB (Hydrophilic-Lipophilic Balance) system for selecting emulsifiers whereby the type of behavior to be expected, rather than the efficiency of emulsification or the amounts of emulsifiers, is derived. This system allows screening of emulsifiers for selection of a number of possible choices, followed by trial. However this system has not been applied to emulsions in which stability to heat is essential.

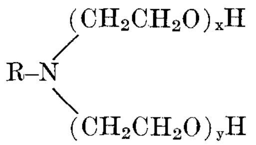
It is realized that the present study does not take into account the many different chemical types of emulsifiers, effect of ionization, and other variables. Representatives of some general classes of widely used emulsifiers have been employed, indicating the applicability of the method of calculation. It is expected that this method, possibly together with that of Griffin, will provide a beginning toward the placing of emulsion preparation on a predictable basis.

In the present report emulsifiers of known composition have been used to determine the specific influence of the lipophilic and hydrophilic groups of these materials on the physical stability of emulsions which have been subjected to sterilization at 121°C. The relationship between the weight percentage of lipophilic and hydrophilic groups and the physical stability of emulsions to heat has been investigated in an effort to provide a basis for calculation of the amount of emulsifiers needed for emulsion formulation of predetermined stability to heat.

For the purpose of this work an homologous series of emulsifiers was desired in which the same lipophilic moiety (alkyl) would be present in all members of the series and in which the hydrophilic moiety (mainly polyoxyethylene) would be variable with respect to the content of ethylene oxide. Such a series would provide emulsifiers in which the weight percentage of the lipophilic and hyldrophilic moieties was variable. By using combinations of the members of such a series together with other emulsifiers in which the weight percentage of lipophilic and hydrophilic groups remained constant, various emulsifying systems were obtained in which the weight percentage of lipophilic and hydrophilic groups were controlled. It therefore was possible to calculate the amounts of lipophilic and hydrophilic groups and the ratio of these groups needed to provide emulsion stability at elevated temperatures. It also was possible to determine whether the sum of the amounts of the individual lipophilic and hydrophilic groups from two or more emulsifiers was as effective in promoting emulsion stability as the same amount of these respective groups derived from a single emulsifier.

Materials

Emulsifiers. The emulsifying agents used to determine the lipophilic-hydrophilic relationship to stability included two emulsifiers of dissimilar type and several members of an homologous series. This latter series consisted of a number of compounds known as Ethomeens, which essentially are tertiary amines with one fatty alkyl group and two polyoxyethylene groups attached to the nitrogen. The acyl moiety of the particular Ethomeens used was the stearyl group. These compounds may be represented as



One of the two individual emulsifiers was a diacetyl tartaric acid ester of a monoglyceride of a fat-forming fatty acid, usually stearic. This product is known by the trade name of TEM. The other emulsifier was a polyoxyethylene-polyoxypropylene nonionic product, with the trade name of Pluronic F68. In each of the latter two emulsifiers the weight percentage of the lipophilic and hydrophilic groups was constant.

In addition to the above emulsifiers, others were used for comparative purposes. These emulsifiers included Ethofats, which are fatty acid esters of polyoxyethylene glycols; Ethomids, which are substituted fatty amides in which two polyoxyethylene groups are attached to the nitrogen; monostearin; soybean phosphatides; and Drumulse 536R, which is partially esterified polyglycerol.

Table I lists the emulsifiers used, their source, and weight percentage of the lipophilic and hydrophilic groups.

Oil. The oil phase in the prepared emulsions consisted of a commerically refined, bleached, winterized, and deodorized cottonseed oil, in the amount of 15% by weight. The interfacial tension of this oil was 14.90 dyne cm. $^{-1}$ at 25°C. (*7*).

TABLE I
Emulsifiers and Source

Emulsifier	Source	Av. mol wt.	Lipophilic moiety	Hydrophilic moiety	POE[a]
			wt. %	*wt. %*	*wt. %*
TEM	Hachmeister Inc.	574.3	49.3	50.7	....
Pluronic F68	Wyandotte Chemicals Corp.	....	*ca.* 20	*ca.* 80	80
Ethomeen 18/15	Armour Chemical Div.	504	47.4	52.6	44
Ethomeen 18/20	Armour Chemical Div.	724	33.0	67.0	61
Ethomeen 18/25	Armour Chemical Div.	944	25.3	74.7	70
Ethomeen 18/60	Armour Chemical Div.	2484	9.6	90.4	89
Ethofat C/15	Armour Chemical Div.	431	46.2	53.8	51
Ethofat C/60	Armour Chemical Div.	2411	8.3	91.7	91
Ethofat 60/60	Armour Chemical Div.	2478	11.4	88.6	88
Ethomid HT/15	Armour Chemical Div.	498	56.4	43.6	44
Ethomid HT/25	Armour Chemical Div.	938	30	70	70
Drumulse 536R	E. F. Drew & Co.	*ca.* 430	66	34	....
Monostearin	Laboratory preparation	358	79.1	20.9	....
Soybean phosphatide	The Glidden Co.	*ca.* 791	71	29	....

[a] POE refers to polyoxyethylene groups.

Aqueous Phase. The aqueous phase was a solution of 5% dextrose in distilled water.

Experimental

Preparation of Emulsions. Pluronic F68 where used, was dissolved in the aqueous phase. All other emulsifiers were incorporated in the oil phase by warming and stirring.

The aqueous phase, in which the dextrose previously had been dissolved, was divided into two approximately equal parts. One of these portions was cycled through a homogenizer at a pressure of about 3,500 psi. The temperature of the liquid was maintained at 65° ± 5°C. The warm oil phase, at 65°C., was added slowly to the cycling aqueous phase until addition was complete. After this emulsion concentrate was cycled twice, the remaining portion of the aqueous phase was added, and two additional cycles were allowed before the emulsion was bottled and sealed. A small portion was reserved for examination.

Steam Autoclaving. Each bottle of emulsion was sterilized at 121°C. for 20 min. Upon removal from the autoclave the bottles were rotated mechanically until cool.

Microscopic Examination. In order to observe the particle size of the completed emulsions, a microscope equipped with an oil immersion lens, which provided a total magnification of 950 diameters was used. A calibrated micrometer allowed direct measurement of particle size. In general, particle size was less than 1 micron, with only a few particles ranging between 2 and 3 microns. Any emulsion in which the particle size exceeded 7 microns in diameter was considered to be unstable to heat.

Mechanical Shock. As a means of determining the resistance of an emulsion to mechanical shock such as might be encountered in shipping, and as a means of obtaining an indication of shelf life, a shaking test was employed in which 50 ml. of emulsion contained in a 100-ml. bottle were shaken at a rapid rate. The bottles were clamped in a horizontal position to the platform of the shaker, which traveled horizontally back and forth at about 250 cycles per minute. All shaking was at room temperature. The particle size of the emulsions was examined at half-hour intervals. An emulsion was considered unstable when the particle size exceeded 7 microns in diameter, in less than 1 hr. of shaking.

Results and Conclusions

The emulsifiers and their amount in each of the emulsion preparations, the calculated content of lipophilic and hydrophilic groups furnished by the emulsifying agents, and the heat stability characteristics of the emulsions are given in Table II.

The following example illustrates the method of calculating the weight percentage of the lipophilic and hydrophilic groups furnished by an individual emulsifier as given in Table II.

Amount of emulsifier based on whole emulsion	0.5	wt. %
Lipophilic moiety of the emulsifier......................	49.3	wt. %
Hydrophilic moiety of the emulsifier..................	50.7	wt. %
Lipophilic content of emulsifier=0.5×49.3%=	0.247	wt. %
Hydrophilic content of emulsifier=0.5×50.7%=	0.254	wt. %

In Table II emulsions 1–36 are arranged in groups. These groups of emulsions range from those in which the emulsifying agents are present individually, mixtures of TEM and individual Ethomeens of variable weight percentages of polyoxyethylene groups, mixtures of TEM and combined Ethomeens, mixtures of TEM and Pluronic F68, and mixtures of TEM, Ethomeens, and Pluronic F68.

The first five emulsions were not stable, indicating that the emulsifiers were not capable of providing stability to autoclaving when used either alone or as mixtures of the same type, at the amounts specified. When these amounts were increased, as in emulsions 6 and 7, stability was achieved. Further, while TEM and Ethomeen 18/25 individually did not provide stability for emulsions 1 and 3, when these same emulsifiers and amounts were combined, as in emulsion 13, the emulsion was stable. It therefore can be stated with some degree of certainty that the effect of the lipophilic and hydrophilic groups of the emulsifier systems was additive. Thus additive characteristics could be observed in subsequent emulsions.

In order to determine the possible relationship between the emulsifying agent and its influence as affecting heat stability of the emulsion, those emulsions from 1 to 23 in each of the above-mentioned groups which were stable to autoclaving were examined with respect to emulsifier composition and lipophilic—hydrophilic content to determine any characteristics common to the stable emulsions.

In emulsions 6 and 7, and 13–23 the emulsifying systems were TEM, Ethomeen, or mixtures of TEM and individual Ethomeens. All of these emulsions were stable, with emulsion 17 classified as on the borderline of stability because of several pinpoint droplets of oil floating on the surface. The total lipophilic groups of each emulsion were at least 0.29 wt. % on a whole emulsion weight basis, and the hydrophilic groups at least 0.57 wt. % on the same basis. The Ethomeens used in emulsions 13–23 were of such chemical composition that polyoxyethylene groups accounted for 70% and 89%, respectively, of the mole weight of these materials.

The characteristics which are common to the stable emulsions 13–23 are: a minimum weight percentage of total lipophilic groups of 0.29%; a minimum weight percentage of total hydrophilic groups of 0.57%. The polyoxyethylene groups of the Ethomeens used account for at least 70% of the mole weight of these emulsifiers; the lipophilic/hydrophilic ratio is about 0.5.

The L/H (lipophilic/hydrophilic) ratio refers to those stable emulsions which contain the minimum amounts of lipophilic and hydrophilic groups, about 0.3 wt. % and 0.6 wt. %, respectively. This may be expressed as L/H, which is equivalent to 0.3/0.6, or 0.5.

If the assumption is made that those characteristics which were found to be common to stable emulsions are the requirements which are necessary for imparting stability to heat, then application of these criteria to those emulsions which were not stable offers a possible explanation for their instability.

Of the emulsions in the group 1–5 the minimum weight percentage requirements of lipophilic and hydrophilic groups were not fulfilled, and in some cases the L/H ratio is low.

Although the lipophilic and hydrophilic groups were present in sufficient amount in all except one case (emulsion 8), and the L/H ratios were adequate, the polyoxyethylene content of the Ethomeen used in emulsions 8–12 was below 70%. This allowed solubility inversion to exert a dominant role, causing instability.

In the five emulsions from 24–28 the total lipophilic content is above 0.30 wt. %. In four of them the total hydrophilic content is at least 0.59 wt. %, and these four were found to be stable. Emulsion 24, with 0.47 wt. % of lipophilic groups, was unstable. Emulsions 24–28 indicate the additive nature of polyoxyethylene groups from two emulsifier sources. Were these groups not additive, there would be insufficient hydrophilic groups to meet minimum requirement.

Pluronic F68 was the sole source of polyoxyethylene groups in emulsions 29 and 30. Although this

TABLE II

Emulsion Composition and Characteristics

Emulsion No.	Emulsifiers and amount (based on whole emulsion)	Lipophilic groups (based on whole emulsion)		Hydrophilic groups (based on whole emulsion)		Stable to autoclaving	Lipophilic/hydrophilic ratio
		Individual	Total	Individual	Total		
	%	*wt. %*	*wt. %*	*wt. %*	*wt. %*		
1	0.5 TEM	0.25	0.25	0.25	0.25	no (oil layer)	1
2	0.19 Ethomeen 18/20	0.06	0.06	0.13	0.13	no (oil layer)	0.58
3	0.46 Ethomeen 18/25	0.12	0.12	0.34	0.34	no (oil layer)	0.35
4	0.20 Ethomeen 18/60 0.09 Ethomeen 18/15	0.02 0.04	0.06	0.18 0.05	0.23	no (broken)	0.32
5	0.20 Ethomeen 18/60 0.33 Ethomeen 18/15	0.02 0.16	0.18	0.18 0.17	0.35	no (broken)	0.51
6	1.5 Ethomeen 18/25	0.38	0.38	1.12	1.12	yes	0.34
7	1.5 TEM	0.74	0.74	0.76	0.76	yes	0.97
8	0.5 TEM 0.19 Ethomeen 18/20	0.25 0.06	0.31	0.25 0.13	0.38	no (oil drops)	0.86
9	0.75 TEM 0.75 Ethomeen 18/15	0.37 0.36	0.73	0.38 0.39	0.77	no (oil layer)	0.97
10	0.75 TEM 0.75 Ethomeen 18/20	0.37 0.25	0.62	0.38 0.50	0.88	no (oil drops)	0.72
11	0.75 TEM 1.0 Ethomeen 18/20	0.37 0.33	0.70	0.38 0.67	1.05	no (oil drops)	0.70
12	1.0 TEM 0.75 Ethomeen 18/20	0.49 0.25	0.74	0.51 0.50	1.01	no (oil drops)	0.75
13	0.5 TEM 0.46 Ethomeen 18/25	0.25 0.12	0.37	0.25 0.34	0.59	yes	0.62
14	0.75 TEM 0.35 Ethomeen 18/25	0.37 0.09	0.46	0.38 0.26	0.64	yes	0.72
15	0.75 TEM 0.6 Ethomeen 18/25	0.37 0.15	0.52	0.38 0.45	0.83	yes	0.64
16	0.75 TEM 0.75 Ethomeen 18/25	0.37 0.19	0.56	0.38 0.56	0.94	yes	0.61
17	0.5 TEM 0.36 Ethomeen 18/60	0.25 0.04	0.29	0.25 0.32	0.57	pinpoint oil droplets, borderline	0.50
18	0.5 TEM 0.46 Ethomeen 18/60	0.25 0.05	0.30	0.25 0.41	0.66	yes	0.45
19	0.5 TEM 0.56 Ethomeen 18/60	0.25 0.05	0.30	0.25 0.51	0.76	yes	0.41
20	0.5 TEM 0.66 Ethomeen 18/60	0.25 0.06	0.31	0.25 0.60	0.85	yes	0.38
21	0.5 TEM 0.74 Ethomeen 18/60	0.25 0.07	0.32	0.25 0.67	0.92	yes	0.34
22	0.5 TEM 1.0 Ethomeen 18/60	0.25 0.10	0.35	0.25 0.90	1.15	yes	0.30
23	0.75 TEM 0.75 Ethomeen 18/60	0.37 0.07	0.44	0.38 0.68	1.06	yes	0.42
24	0.5 TEM 0.2 Ethomeen 18/60 0.09 Ethomeen 18/15	0.25 0.02 0.05	0.32	0.25 0.18 0.04	0.47	no (oil drops)	0.67
25	0.5 TEM 0.2 Ethomeen 18/60 0.33 Ethomeen 18/15	0.25 0.02 0.16	0.43	0.25 0.18 0.17	0.60	yes	0.71
26	0.5 TEM 0.3 Ethomeen 18/60 0.1 Ethomeen 18/20	0.25 0.03 0.03	0.31	0.25 0.27 0.07	0.59	yes	0.52
27	0.5 TEM 0.5 Ethomeen 18/60 0.05 Ethomeen 18/25	0.25 0.05 0.01	0.31	0.25 0.45 0.04	0.74	yes	0.42
28	0.75 TEM 0.25 Ethomeen 18/60 0.5 Ethomeen 18/25	0.37 0.03 0.13	0.53	0.38 0.22 0.37	0.97	yes	0.54
29	0.3 TEM 0.75 Pluronic F68	0.15 0.15	0.30	0.15 0.60	0.75	yes	0.40
30	0.5 TEM 0.75 Pluronic F68	0.25 0.15	0.40	0.25 0.60	0.85	yes	0.47
31	0.5 TEM 0.18 Ethomeen 18/25 0.12 Pluronic F68	0.25 0.05 0.02	0.32	0.25 0.13 0.10	0.48	no (oil layer)	0.66
32	0.5 TEM 0.25 Ethomeen 18/25 0.15 Pluronic F68	0.25 0.06 0.03	0.34	0.25 0.19 0.12	0.56	yes	0.63
33	0.5 TEM 0.25 Ethomeen 18/25 0.3 Pluronic F68	0.25 0.06 0.06	0.37	0.25 0.19 0.24	0.68	yes	0.56
34	0.5 TEM 0.25 Ethomeen 18/25 0.39 Pluronic F68	0.25 0.06 0.08	0.39	0.25 0.19 0.31	0.75	yes	0.54
35	0.75 TEM 0.35 Ethomeen 18/25 0.15 Pluronic F68	0.37 0.09 0.03	0.49	0.38 0.26 0.12	0.76	yes	0.64
36	1.0 TEM 0.5 Ethomeen 18/20 0.3 Pluronic F68	0.49 0.17 0.06	0.72	0.51 0.33 0.24	1.08	yes	0.66
37	0.5 TEM 0.5 Ethofat C/60	0.25 0.09	0.34	0.25 0.41	0.66	no (oil globule)	0.51
38	0.5 TEM 0.5 Ethofat 60/60	0.25 0.06	0.31	0.25 0.44	0.69	yes	0.45
39	0.75 Ethofat 60/60 0.4 Ethomid HT/15	0.09 0.23	0.32	0.66 0.17	0.83	no (broken)	0.38
40	0.8 Ethofat C/60 0.5 Ethofat C/15	0.07 0.23	0.30	0.73 0.27	1.00	no (broken)	0.30
41	0.5 TEM 0.6 Ethomid HT/25	0.25 0.18	0.43	0.25 0.42	0.67	yes	0.64
42	0.5 TEM 0.8 Ethomid HT/15	0.25 0.45	0.70	0.25 0.35	0.60	no (oil globule)	1.16

Emulsion No.	Emulsifiers and amount (based on whole emulsion)	Lipophilic groups (based on whole emulsion)		Hydrophilic groups (based on whole emulsion)		Stable to autoclaving	Lipophilic/hydrophilic ratio
		Individual	Total	Individual	Total		
	%	*wt. %*	*wt. %*	*wt. %*	*wt. %*		
43	0.5 TEM	0.25		0.25			
	0.3 Ethomid HT/15	0.17		0.13			
	0.75 Pluronic F68	0.15	0.57	0.60	0.98	yes	0.58
44	1.0 Monostearin	0.79		0.21			
	0.3 Pluronic F68	0.06	0.85	0.24	0.45	no (broken)	1.9
45	1.2 Drumulse 536R	0.79		0.41			
	0.2 TEM	0.10		0.10	0.67		
	0.2 Pluronic F68	0.04	0.93	0.16		yes	1.23
46	1.2 Soy. Phosphatide	0.85		0.35			
	0.3 Pluronic F68	0.06	0.91	0.24	0.59	yes	1.54

emulsifier agent provided some lipophilic groups, they (polyoxypropylene) are of a different nature from the lipophilic stearoyl group of TEM. These emulsions were stable, with about the same weight percentage and ratio of lipophilic and hydrophilic groups as in other stable emulsions. It therefore would appear that the dissimilar lipophilic and hydrophilic groups of these emulsifiers are additive and that the weight percentage of lipophilic and hydrophilic groups required are about the same as for those emulsions in which part of the lipophilic and hydrophilic groups were supplied by Ethomeens.

Emulsions 31–36 indicate the apparently additive characteristics of three emulsifiers of different types. In all of these emulsions the lipophilic content is above 0.30 wt. %. The hydrophilic content of emulsion 31 is 0.48%, lower than the others, and this emulsion is not stable. The hydrophilic content of the other emulsions is adequate. The L/H ratio of the stable emulsions appears to be sufficient as well as the polyoxyethylene content of the Ethomeens used.

In order to determine whether the relationships which were found applicable to Ethomeen emulsifiers would exist for other emulsifiers differing from Ethomeens in type and in chain length of the acyl group, Ethofats and Ethomids were employed. These two types of emulsifiers are nonionic. The acyl groups of the Ethofat emulsifiers used were variable with respect to length of carbon chain, being derived either from coconut oil fatty acids or from saturated C_{18} acids. The acyl group of the Ethomid products was derived from hydrogenated tallow. The polyoxyethylene content varied in the respective products. The properties of emulsions 37–43, prepared with these products, are given in Table II.

Emulsions 38, 41, and 43 were stable. Each of these meets the previously indicated minimum weight percentage requirements of lipophilic and hydrophilic groups, L/H ratio, and weight percentage of polyoxyethylene groups in the emulsifiers. Emulsion 37 was not stable to heat although similar to stable emulsion 38 in weight percentages of lipophilic and hydrophilic groups. Emulsions 37 and 38 contain the same amounts of TEM and Ethofats, but their respective Ethofat emulsifiers differ in the number of carbon atoms of the acyl groups. The acyl group of Ethofat C/60, in emulsion 37, contains fewer carbon atoms than does the acyl group of Ethofat 60/60 of emulsion 38. This indicates that an acyl group of 12 carbon atoms is insufficient to impart autoclaving stability at the levels employed. This would also apply to emulsion 40, which probably was unstable because of short chain acyl groups and low polyoxyethylene content of the Ethofat C/15.

In emulsions 39 and 42 the number of carbon atoms in the acyl groups of the emulsifiers is 18, and the amounts of lipophilic and hydrophilic groups meet the minimum requirements. However the polyoxyethylene content of the Ethomids used in each is low. In emulsion 39 the polyoxyethylene content furnished by the Ethofat is insufficient to prevent solubility inversion of the Ethomid used, hence the emulsion is unstable. In emulsion 42 the solubility inversion of the emulsifier because of insufficient polyoxyethylene content resulted in instability on autoclaving. In this connection it seems of interest that the polyoxyethylene content of emulsion 43 is mostly furnished by the Pluronic F68 and is sufficient to promote stability.

It might be expected that emulsifier systems containing emulsifying agents different from those used in the present study would behave in a similar manner. This observation was checked in a limited way with three emulsions. The emulsifiers chosen as the major components of the emulsifying systems were purified monostearin, soybean phosphatide, and Drumulse 536R. Monostearin has a high weight percentage of lipophilic groups and correspondingly low hydrophilic content. The lipophilic-hydrophilic contents and molecular weights of the phosphatide and Drumulse product were calculated as average values. These emulsifiers were incorporated into emulsions 44–46, as shown in Table II.

The content of lipophilic groups in emulsion 44 was above the minimum requirement previously found for Ethomeen systems, but the hydrophilic content was low. The emulsion was not stable. Emulsions 45 and 46 were stable. The combined weight percentage of lipophilic and hydrophilic groups of the emulsifiers of these systems meet the minimum requirements of all previous emulsions which were stable, and these requirements therefore seem applicable to emulsifiers of these types.

Since the present investigation dealt primarily with the heat stability of emulsions, there was no attempt to determine the effectiveness of a variety of emulsifiers in imparting resistance to breakage of an emulsion by mechanical shock. However several representative heat-stable emulsions were shaken as described. The results of this shaking test are given in Table III.

TABLE III

Effect of Shaking on Particle Size of Emulsions

Emulsion No.	Total lipophilic groups	Total hydrophilic groups	Stability to growth of particle size	Lipophilic/hydrophylic ratio
	%	%		
18	0.30	0.66	less than 1 hr.	0.45
20	0.32	0.84	less than 1 hr.	0.38
26	0.31	0.59	less than 1 hr.	0.52
13	0.37	0.59	1 hr.	0.62
15	0.53	0.82	1–2 hrs.	0.64
16	0.57	0.93	1–2 hrs.	0.61
45	0.93	0.67	over 2 hrs.	1.23
46	0.91	0.59	over 2 hrs.	1.54

Those emulsions which resisted breakage (growth of particle size to in excess of 7 microns in diameter) by shaking for less than 1 hr. had but little excess of lipophilic content over the minimum requirement. As the lipophilic content increased and therefore the L/H ratio, as in emulsions 13–16, the resistance to particle size growth also increased. A further increase of the L/H ratio to above 1, as in emulsions 45 and 46, greatly increased the stability to shaking. It would appear that the content of lipophilic groups and the L/H ratio must be high in order to obtain shaking stability and that the hydrophilic content is not a primary consideration for imparting this property.

The conclusion reached is that with a given system of emulsifiers a definite minimum content of both lipophilic and hydrophilic groups is necessary for heat stability of emulsions. The content of such groups seems to be an additive total of the weight percentage of lipophilic and hydrophilic groups furnished by the individual emulsifying agents. By making a choice of suitable emulsifiers and determining the weight percentage of lipophilic and hydrophilic groups which will be furnished by each emulsifier, the amount of emulsifiers needed to prepare fat emulsions which are stable to heat and which resist breakage by mechanical shock can be calculated.

Summary

When a given system of emulsifiers of known compositions and molecular weights was employed, it was found that in order for fat emulsions of 15% oil content to be stable to the heat required for sterilization, the emulsifiers must meet definite requirements. Minimum weight percentage of total lipophilic groups should be 0.29%; minimum weight percentage of total hydrophilic groups should be 0.57%; the polyoxyethylene groups of emulsifiers containing such groups should account for at least 70% of the mole weight of these emulsifiers; the lipophilic/hydrophilic ratio should be about 0.5. The minimum content of lipophilic and hydrophilic groups was found to be an additive total of these groups as provided by the complete emulsifying system whether composed of individual or multiple emulsifying agents and whether of similar or dissimilar functional groups.

With the emulsifiers used, an acyl group greater in length than 12 carbon atoms was found to be necessary to prepare cottonseed oil emulsions which were stable to heat.

Resistance of emulsions to breakage by mechanical shock was imparted by a rather large amount of lipophilic groups, so that the lipophilic/hydrophilic ratio was 1 or over.

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Report of the Smalley Committee, 1957-58

AGAIN THIS SEASON nine different types of samples were distributed by seven subcommittees. These included cottonseed, soybeans, peanuts, meal, vegetable oils, tallow and grease, glycerine, drying oils, and edible fats. In all, 4,497 samples were distributed to 516 collaborators, and approximately 16,000 results were tabulated. Table I shows the distribution and participation. There was a 23% increase in participation in 1957 over 1956 and a 5% increase in 1958 over the 1956-57 season. A detailed account of the expenses has been given to the Governing Board. In all cases a detailed report has been given to the collaborators, summarizing the work and listing the relative standing, based on our various grading systems. It is fitting to express our thanks to various subcommittee members for their contributions, especially to:

TABLE I

	Number of collaborators	Number of samples	Number of determinations per sample
Cottonseed	51	10	6
Soybeans	37	10	2
Peanuts	12	7	5
Meal	134	15	3
Vegetable oils	96	6	3
Tallow and grease	90	5	7
Glycerine	23	5	5–3
Drying oils	17	6	5
Edible fats	56	5	14

K. H. Fink, Armour and Company, for tabulating and mailing the tallow and grease results and calculating the final grades, also for assisting with the edible fat calculations;
F. R. Earle, Northern Regional Research Laboratory, for tabulating and mailing the soybean oil results;
C. L. Hoffpauir, Southern Regional Research Laboratory, for tabulating the cottonseed oil results;
R. A. Decker, Armour and Company, for calculating the final grades on the vegetable oils;
Oscar Wilkins, now of Barrow-Agee Laboratories, for preparing and shipping the vegetable oils and the tallow and grease samples;
Jack Rini, HumKo Company, for selecting the vegetable oil samples;
T. R. Bresnahan, Darling and Company, for selecting and shipping the bulk tallow and grease samples;
G. C. Henry, Law and Company, for handling the preparation and distribution of the edible fat samples;
W. J. Miller, Procter and Gamble, for the preparation and distribution of the edible fat samples;
Bart Teasdale, Canada Packers Ltd., for re-mailing the vegetable oil and tallow and grease samples in Canada.

Reasonably sound grading systems have been established in all the series, and certificates of proficiency will be presented this year in all categories. The Smalley awards presented this year were as follows:

Cottonseed. With 51 chemists participating, first place was given to P. D. Cretien, Texas Testing Laboratory, Dallas, Tex., with a grade of 99.70; second place to E. R. Hahn, Hahn Laboratories, Columbia, S. C., with 99.40; and honorable mention to A. H. Grimes, Barrow-Agee Laboratory, Decatur, Ala., with 98.08.

Soybean. With 37 chemists participating, first place went to J. G. Bowling, Woodson-Tenent Laboratory, Des Moines, Ia., with a grade of 100; second place to Mr. Hahn, with 99.40; and honorable mention to E. H. Tenent Jr., Woodson-Tenent Laboratory Memphis, with 99.10.