

# Some observations on the use of fatty alcohols and fatty acids to increase the consistency of oil-in-water emulsions

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A range of fatty alcohols and fatty acids of different chain lengths and chemical configuration has been examined to determine which of these may be usefully employed to increase the consistency of liquid paraffin-in-water emulsions stabilized by condensed complex films. Of the alcohols, a straight chain of 16 carbon atoms (cetyl alcohol) or a physical mixture of straight chains of 16 and 18 carbon atoms (cetostearyl alcohol) gave maximum bodying action. To a lesser extent a straight chain of 14 carbon atoms (myristyl alcohol) and in some cases a straight chain of 12 carbon atoms (lauryl alcohol) also increased the consistency of emulsions. Other homologues ( $C_8$ ,  $C_{10}$  and  $C_{18}$ ), unsaturated or branched chain alcohols and fatty acids were, in general, found to be of little value for this purpose.

Martin (1960) made the broad statement that fatty alcohols and fatty acids could be used to increase the consistency of oil-in-water emulsions. Both the pharmaceutical and cosmetics industries employ a wide range of these materials but only oleic acid, stearic acid and cetostearyl alcohol are the subjects of official monographs. The latter is well known as a consistency improver and is used in conjunction with sodium lauryl sulphate, cetrimide or cetomacrogol 1000 to form self-bodying waxes. This paper is concerned with investigations into which of the fatty alcohols and acids could usefully be employed to increase the consistency of oil-in-water emulsions stabilized by condensed complex films.

## EXPERIMENTAL

*Materials.* Octyl, decyl, lauryl, myristyl, cetyl and stearyl alcohols (Laurex 8-18) (from Cyclochemicals Ltd., London), oleyl alcohol (BDH, Poole), octyldodecyl alcohol (Henkel International GmbH, Dusseldorf), octoic and decaic acids (BDH, Poole), lauric, myristic, palmitic, stearic, behenic and erucic acids (Univol U. 314B, 320, 332, 334, 344 and 342) (Universal Oil Co. Ltd., Hull) were all commercial grades and were used without purification. All other materials conformed to the requirements of the B.P. or B.P.C.

*Methods.* These are as previously described (Talman, Davies & Rowan, 1967, 1968).

## RESULTS AND DISCUSSION

The apparent viscosities and static yield values (as defined by Talman & others, 1967) of emulsions containing a range of fatty alcohols together with cetomacrogol 1000 or cetrimide at 0.5 or 5.0% w/w concentrations are shown in Table 1. It will be

Table 1. Apparent viscosities ( $\eta_{100}$  in centipoises) and static yield values [SYV in  $\text{mNm}^{-2}$  (dynes/cm<sup>2</sup>)] of 50% w/w liquid paraffin emulsions containing varying concentrations of fatty alcohols (% w/w) with 0.5 and 5.0% w/w cetomacrogol 1000 or cetrimide

Fatty alcohol	Cetomacrogol 1000 (0.5%)										Cetrimide 0.5%													
	1% SYV					Concentration of fatty alcohol in emulsion					1% SYV					Concentration of fatty alcohol in emulsion								
	$\eta_{100}$	2%	4%	6%	8%	10%	2%	4%	6%	8%	10%	$\eta_{100}$	2%	4%	6%	8%	10%	2%	4%	6%	8%	10%		
Oleyl alcohol	11	0	16	0	18	0	21	0	25	0	27	0	13	0	13	0	14	0	20	0	21	0	21	0
Octyl(dodecyl) alcohol	14	0	14	0	19	0	20	0	25	0	29	0	10	0	10	0	17	0	25	0	30	0	30	0
Octyl alcohol	14	0	14	0	17	0	18	0	22	0	24	0	14	0	16	0	16	0	24	0	34	0	34	0
Decyl alcohol	15	0	16	0	16	0	17	0	21	0	24	0	14	0	19	0	20	0	24	0	30	0	30	0
Lauryl alcohol	15	0	15	0	15	0	18	0	21	0	28	0	39	151	64	352	58	477	74	503	691	94	30	754
Myristyl alcohol	11	0.25%	23	2%	74	4%	302	128	1131	166	2512	229	10%	12	2%	553	87	628	190	583	300	3517	334	6030
Cetyl alcohol	13	0.25%	18	0.75%	57	1.5%	226	156	854	316	2456	447	0.25%	14	0.75%	0	61	377	139	1005	265	2362	361	6287
Cetostearyl alcohol	11	0.15%	15	0	51	0.75%	276	126	905	275	2337	468	15	0	46	251	130	1005	269	2412	638	6659	638	6659
Stearyl alcohol	14	0	11	0	18	0	88	452	120	704	4.0%	13	0.15%	0	0.25%	0	20	0	49	1.5%	125	829	177	1508
Oleyl alcohol	33	0	37	x	44	x	44	x	53	x	64	x	76	x	82	x	82	x	139	x	186	1382	228	1809
Octyl(dodecyl) alcohol	32	0	36	x	44	x	44	x	51	x	54	x	70	x	70	x	70	x	139	x	38	121	377	
Octyl alcohol	35	0	40	x	40	x	48	x	54	x	54	x	65	x	65	x	65	x	139	x	38	121	377	
Decyl alcohol	31	0	33	x	38	x	47	x	50	x	50	x	61	x	61	x	61	x	139	x	38	121	377	
Lauryl alcohol	28	0	22	0	46	x	55	x	65	x	65	x	83	x	83	x	83	x	139	x	38	121	377	
Myristyl alcohol	30	0.25%	50	2%	94	4%	226	133	6%	578	320	2375	324	10%	22	0.25%	0	4%	879	329	4184	8%	10%	x
Cetyl alcohol	35	0.25%	40	0.75%	66	1.5%	226	84	2.5%	201	128	4.0%	377	433	21	0.25%	0	1.5%	0	44	2.5%	94	376	363
Cetostearyl alcohol	33	0	36	0	63	0	63	x	94	151	141	276	393	3015	16	0	20	0	44	101	87	126	343	2952
Stearyl alcohol	30	0	35	0	40	0	64	1.5%	95	201	133	251	18	0.15%	20	0.25%	0	0.75%	0	26	41	2.5%	69	188

∞ = Mean static yield value. x = Pseudoplastic. X = Traces uninterpretable. / = Sample contained waxy particles.

noted that although the type and concentration of the water-soluble surfactant affected the absolute magnitude of the flow parameters, the only alcohols that produced a marked increase in the consistency of preparations were cetyl and ceto-stearyl alcohols and to a lesser extent myristyl alcohol.

Emulsions containing more than 4.0% w/w stearyl alcohol were difficult to prepare and as they contained waxy particles of the alcohol their apparent viscosities and static yield values could not be determined. Preparation of these samples at 70°, i.e. 10° above that used in the standard procedure, did not reduce the incidence of waxy particles. As noted previously (Talman & others, 1967) products containing lauryl alcohol and cetrimege were thicker than corresponding emulsions prepared with lauryl alcohol and cetomacrogol 1000. Increasing amounts of oleyl, octyl-dodecyl, octyl and decyl alcohols with either surfactant at 0.5% w/w gave products of slightly increased viscosity but all were Newtonian fluids. Comparison of these results with those where the oleyl alcohol content was kept constant but the quantity of liquid paraffin altered, suggested that the rise in viscosity could be attributed to an increase in total disperse phase (Fig. 1). With all four alcohols, cetomacrogol 1000

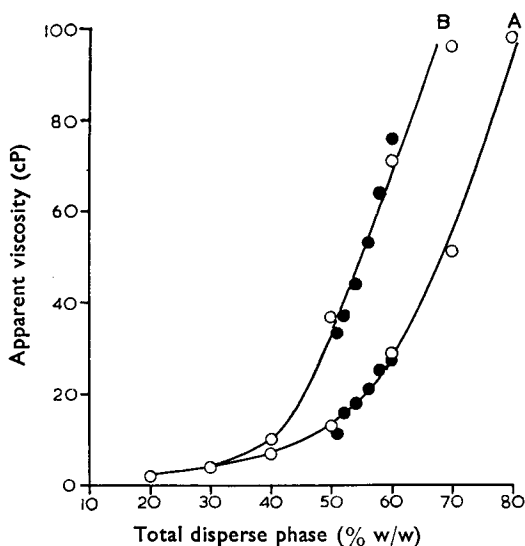


FIG. 1. Effect of varying total disperse phase (% w/w) on apparent viscosity of emulsions containing 0.5 (A) or 5.0% w/w (B) cetomacrogol 1000. ○, 2% w/w oleyl alcohol with varying amounts of liquid paraffin. ●, 50% w/w liquid paraffin and varying amounts of oleyl alcohol.

(5.0% w/w) produced emulsions of greater apparent viscosity than those containing 0.5% w/w; some were pseudoplastic and the results were again comparable with those from preparations of constant fatty alcohol content but varying disperse phase. This too has been illustrated in Fig. 1. As reported previously (Talman & others, 1968), the data for emulsions containing oleyl alcohol could not be correlated with emulsifier concentration, phase volume ratio or globule size distribution by expressions of the type proposed by Sherman (1959, 1963). Octyl and decyl alcohols were included to extend the range of chain lengths investigated. In addition to their having little value as consistency improvers, both have unpleasant odours and are therefore of little interest in practice.

The preparation of products containing high concentrations of  $C_8 - C_{14}$  straight chain alcohols together with 5.0% w/w cetrimide gave emulsions so viscous during the initial stages of preparation that they could not be passed four times through the Q.P. homogenizer as was the normal procedure. The rheograms obtained with the Ferranti-Shirley viscometer were irregular, neither a reliable apparent viscosity nor static yield value could be determined from the traces and visual examination of the samples suggested that this irregularity might be due to marked visco-elastic properties. Visco-elasticity has been observed and measured in related systems by Barry (1968) and Davis (1969). Continuous shear methods are not applicable to the measurement of the fundamental rheological parameters of visco-elastic systems (Warburton & Barry, 1968). Nevertheless, as noted by Barry (1969), instruments employing such methods, e.g. the Rotovisko and Ferranti-Shirley viscometers, are valid tools for investigating trends in the behaviour of a series of samples. As equipment for examining elastic properties was not available this latter aspect of the flow behaviour of our samples could not be studied.

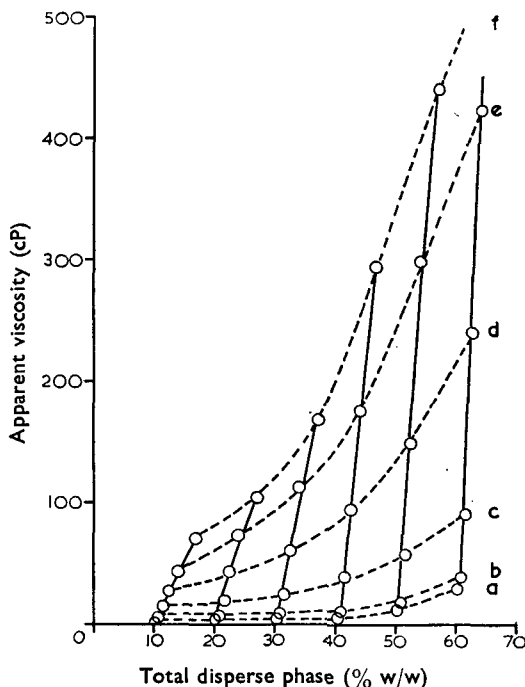


FIG. 2. Effect of varying total disperse phase on apparent viscosity of emulsions prepared with cetostearyl alcohol and 0.5% w/w cetomacrogol 1000.  $\circ$ — $\circ$ , Constant liquid paraffin content.  $\circ$ — $\circ$ , Constant cetostearyl alcohol content. a, b, c, d, e and f are 0.25, 0.75, 1.5, 2.5, 4.0 and 7.0% w/w cetostearyl alcohol in the emulsion.

The effects of varying the amounts of both cetostearyl alcohol and liquid paraffin on the apparent viscosities and static yield values of a range of emulsions are shown in Figs 2 and 3 respectively. They clearly show that increasing the total disperse phase with this alcohol had a greater effect on the flow parameters than the addition of a comparable amount of liquid paraffin. This may be contrasted with the behaviour of emulsions containing oleyl alcohol (Fig. 1). The latter amphiphile does not form a gel in the continuous phase (Talman & others, 1967).

Table 2. Apparent viscosities ( $\eta_{100}$  in centipoises) and static yield values [SYV in  $\text{mNm}^{-2}$  (dynes/cm<sup>2</sup>)] of 50% liquid paraffin emulsions containing varying concentrations of fatty acids (% w/w) with 0.5 and 5.0% w/w cetomacrogol 1000 or cetrimide

Fatty acid	Cetomacrogol 1000 (0.5%)										Cetrimide (0.5%)													
	0.25%		1.0%		2.0%		3.0%		5.0%		7.0%		0.25%		1.0%		2.0%		3.0%		5.0%		7.0%	
	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV
Oleic acid	12	0	10	0	12	0	13	0	16	0	17	0	19	0	20	0	10	0	10	0	12	0	15	0
Erucic acid	10	0	12	0	14	0	17	0	19	0	19	0	18	0	19	0	13	0	15	0	16	0	19	0
Octoic acid	12	0	14	0	12	0	12	0	15	0	13	0	16	0	16	0	9	0	9	0	12	0	13	0
Decoic acid	11	0	12	0	10	0	13	0	13	0	15	0	19	0	19	0	12	0	14	0	17	0	17	0
Lauric acid	10	0	14	0	9	0	13	0	15	0	13	0	13	0	13	0	12	0	12	0	16	0	20	0
Myristic acid	10	0	11	0	13	0	13	0	13	0	13	0	13	0	13	0	13	0	12	0	16	0	16	0
Palmitic acid	11	0	13	0	14	0	14	0	14	0	14	0	14	0	14	0	13	0	12	0	16	0	16	0
Stearic acid	10	0	14	0	15	0	15	0	15	0	15	0	15	0	15	0	13	0	13	0	16	0	16	0
Behenic acid	10	0	14	0	15	0	15	0	15	0	15	0	15	0	15	0	13	0	13	0	16	0	16	0
	27	0	29	0	27	0	27	0	30	0	27	0	27	0	27	0	27	0	23	0	20	0	26	0
Oleic acid	26	0	25	0	27	0	27	0	37	0	37	0	44	0	44	0	20	0	23	0	26	0	78	x
Erucic acid	30	0	31	0	31	0	31	0	34	0	34	0	45	0	45	0	22	0	28	0	45	0	185	x
Octoic acid	9	0	27	0	30	0	32	0	35	0	35	0	46	0	46	0	29	0	31	0	107	x	179	x
Decoic acid	27	0	29	0	32	0	33	0	35	0	35	0	41	0	41	0	25	0	38	0	137	x	179	x
Lauric acid	26	0	27	0	32	0	36	0	36	0	36	0	41	0	41	0	46	0	46	0	314	x	4020	x
Myristic acid	25	0	29	0	40	0	42	0	42	0	42	0	91	x	113	x	27	0	84	0	152	603	250	4020
Palmitic acid	27	0	42	x	72	x	104	x	104	x	104	x	91	113	113	x	17	0	53	x	286	1809	293	4146
Stearic acid	27	0	30	0	40	0	40	0	49	0	49	0	49	0	49	0	29	0	52	x	92	603	200	2198
Behenic acid	27	0	30	0	40	0	40	0	49	0	49	0	49	0	49	0	29	0	54	0	92	603	200	2198

/ = Samples unstable and contained waxy particles. x = Pseudoplastic. X = Traces uninterpretable.

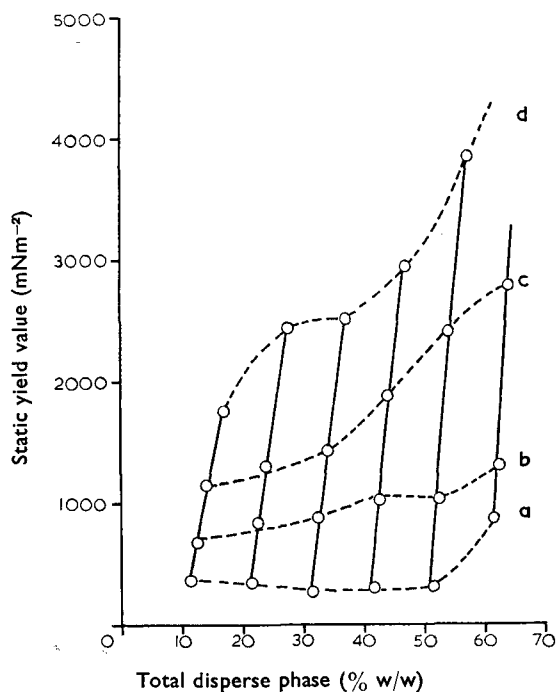


FIG. 3. Effect of varying total disperse phase on static yield value of emulsions prepared with cetostearyl alcohol and 0.5% w/w cetomacrogol 1000.  $\circ$ — $\circ$ , Constant liquid paraffin content.  $\circ$ — $\circ$ — $\circ$ , Constant cetostearyl alcohol content. a, b, c and d are 1.5, 2.5, 4.0 and 7.0% w/w cetostearyl alcohol in the emulsion.

Table 2 shows data for comparable emulsions containing a range of fatty acids. The flow properties of preparations containing 5.0% w/w cetrinide were similar to those made with the alcohols; high concentrations of myristic, palmitic or stearic acids produced the most marked increases in consistency. However, such preparations are of little use for topical application as high concentrations of cetrinide can cause drying and sensitization of the skin (Martindale, 1967). It was only with 5.0% w/w cetrinide that the acids could be induced to form gels (Table 3) comparable in strength to those produced by the alcohols and which were reported elsewhere (Talman & others, 1967, 1968).

Table 3. Apparent viscosities ( $\eta_{100}$  in centipoises) and static yield values [SYV in  $\text{mNm}^{-2}$  (dynes/cm<sup>2</sup>)] of gels containing 10% w/w fatty acids and 0.5 or 5.0% w/w cetomacrogol 1000 or cetrinide

Fatty acid	Cetomacrogol 1000 (% w/w)				Cetrinide (% w/w)			
	0.5		5.0		0.5		5.0	
	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV	$\eta_{100}$	SYV
Oleic acid .. ..	1	0	4	0	1	0	7	0
Erucic acid .. ..	1	0	3	0	1	0	41	x
Lauric acid .. ..	/	/	/	/	17	239	165	1897
Myristic acid ..	/	/	/	/	14	x	102	1168
Palmitic acid ..	/	/	/	/	/	/	36	415
Stearic acid .. ..	/	/	/	/	/	/	18	176
Behenic acid .. ..	/	/	/	/	/	/	/	/

/ = Samples contained waxy particles.

x = Pseudoplastic.

Samples with high concentrations of octoic, decoic or lauric acids and 5.0% w/w cetrimide were difficult to prepare on account of the high viscosity of the mixture of phases before homogenization and the rheograms could not be interpreted due to visco-elastic effects. Waxy particles were present in emulsions with the 5.0% w/w concentration of cetrimide and more than 5.0% w/w behenic acid. The phases employed for the preparation of emulsions containing 0.5% w/w cetrimide or 0.5 or 5.0% w/w cetomacrogol 1000 together with the acids did not readily emulsify whilst the final products were either thin fluids or contained waxy particles. Here too, preparation at 70° did not yield products free from particles of fatty acid. It should be remembered that stearic and some other acids can be used in a partially neutralized form to produce bodied emulsions. Spalton (1953) gives a number of examples but such products were not included in the present investigation.

These results demonstrate that contrary to Martin's general statement on the ability of fatty acids and alcohols to increase the consistency of emulsions, only a limited number of these are useful for this purpose. The fluid amphiphiles have little or no bodying action whilst some solid amphiphiles give rise to waxy particles in the aqueous phase of the emulsion. The actual self-bodying mechanism involved has not been investigated for the preparations discussed here, but it is reasonable to suppose that transfer of fatty acid or alcohol from the oil to aqueous phase took place as was postulated by Talman & others (1967) for cetostearyl alcohol and, in some cases, lauryl alcohol. If transfer was followed by interaction with the surfactant in the aqueous phase a semi-solid preparation was obtained, but where this interaction did not occur waxy particles of amphiphile were formed. The requirements for self-bodying action, based on the concepts of amphiphile transfer to and interaction in the aqueous phase of an emulsion, have been discussed by Barry (1969). Further studies (Talman & Rowan, 1970) suggest that self-bodying action is related to the penetrability of the fatty amphiphile by the surfactant. Palmitic acid (m.p. 63–64°) is not penetrated by a 0.5% w/w cetrimide solution nor does it interact with that solution at temperatures above its melting point. This explains the occurrence of waxy particles in corresponding emulsions even when a temperature of 70° is used for preparation. Generally, penetration is more likely to occur and is more extensive with the low molecular weight ionic surfactants at high concentration and this is reflected in the properties of the emulsions.

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