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# Effects of Tween and Span Group Emulsifiers on the Stability of o/w Emulsions[1]

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The effect of blending Tween and Span emulsifiers on emulsion formation were investigated, and the HLB values required to produce stable o/w emulsions are considered in detail.

The emulsifiers used were the commercial grade Tween series and Span series, and the oil used was a liquid paraffin (dispersed phase). Emulsion stability was measured by four methods: with a measuring cylinder, a Coulter counter, a turbidimeter, and a rheometer.

The following results were obtained; (1) The rate of separation increased in the following order with blended emulsifiers: Tween 80+Span 20, Tween 20+Span 20, Tween 40+Span 20, and Tween 20+Span 80. However, the emulsion prepared with Tween 20+Span 80 was unstable over the whole range of HLB. (2) The o/w emulsions prepared using mixtures of Tween and Span showed a maximum droplet number at an HLB value of 11.0. (3) The viscosity of the emulsion prepared with Tween alone was clearly smaller than those obtained with blended emulsifiers.

**Keywords**——adsorption; agitator; Coulter counter; emulsion stability; emulsifier; HLB system; rheometer; Span series; turbidimeter; Tween series

The hydrophile-lypophile balance (HLB) system developed by Griffin[3] is a very valuable tool for the selection of emulsifiers. In the preparation of emulsions, an emulsifier mixture combining a low-HLB emulsifier with a high-HLB one usually yields a more stable emulsion than does a single emulsifier,[4] even if it gives the same HLB number as the mixture. Accordingly, selection of the most suitable emulsifier, including an appropriate combination of several emulsifying agents, is of fundamental importance.

The purpose of the present work was to investigate the effect of the blending of Tween and Span emulsifiers on emulsion formation and to consider in detail the HLB value required for the stability of o/w emulsions.

## Experimental

**Equipment**——A sketch of the apparatus used in the preparation of emulsions was presented in our previous paper.[5] The clear acrylate resin agitation tank with 4 baffles is 150 mm in diameter and 210 mm in depth. The 49.0 mm long stainless-steel agitation impeller is of a standard Rushton type with 6 blades. The tank was sealed with an acrylate resin disk to prevent the access of air, and it was surrounded by a water jaket in order to keep the temperature at 20.0°. The rate of revolution of the impeller was constant at 812 rpm, and the agitation period was fixed at 60 min.

**Preparation of Emulsion**——The emulsifiers used were the commercial grade Tween series (polyoxyethylene sorbitan ester), Tween 20, 40, 80, and 81, and the Span series (sorbitan carboxyl ester), Span 20 and 80 (Kao-Atlas Co., Tokyo), and the oil used was liquid paraffin (Taisei Chemical Industry, Tokyo). The physical properties of the emulsifiers are summarized in Table I.

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1) S. Noro, A. Takamura, and T. Minowa, Presented at the 31st Symposium of Colloid and Surface Chemistry (Chemical Society of Japan), Toyama, October, 1978.
2) Location: *1-22-1, Yato-cho, Tanashi-shi, Tokyo 188, Japan.*
3) W.C. Griffin, *Off. Dig. Fed. Paint Varn. Prod. Clubs.*, **28**, 446 (1956).
4) J.A. Michael and L.L. John, *J. Pharm. Sci.*, **65**, 216 (1976).
5) S. Noro, A. Takamura, and M. Koishi, *Chem. Pharm. Bull.* (Tokyo), **27**, 309 (1979).

In preparing o/w emulsions, the emulsifiers used were blends of Tween and Span, or Tween alone, with HLB values in the range of 9.0—15.0. The emulsifiers used in blends were Tween 20+Span 80. The HLB values were adjusted to 9.5, 10.0, 11.0, 12.0, 13.0, and 14.0; in addition, the weight ratios of Tweens and Spans are listed in Table II.

Before starting emulsification, Tween was always dissolved in the aqueous phase, and Span in the oil phase. The total emulsifier concentration in each emulsion was kept constant at 5.1%. The emulsions always contained 38.6% of the dispersed phase.

The agitation tank was filled with 1375 g of distilled water as the continuous phase. The impeller was positioned in the center of the tank. Liquid paraffin (943 g) was gently placed on the middle of the impeller as the dispersed phase. Before mixing, the tank was sealed with an acrylate resin disk to exclude air. The emulsified liquid was sampled with a glass tube (5 mm) 60 min after starting agitation.

The interfacial tension between the oil and water was measured by the ring method⁶⁾ and the specific gravity was measured with a hydrometer at 20.0±0.1°.

Table I. Physical Properties of Emulsifiers

| Emulsifier | Chemical name | HLB value | Saponification value |
|---|---|---|---|
| Span 80 | Sorbitan monooleate | 4.3 | 145—160 |
| Span 20 | Sorbitan monolaurate | 8.6 | 158—170 |
| Tween 81 | Polyoxyethylene sorbitan monooleate | 10.0 | 96—104 |
| Tween 80 | Polyoxyethylene sorbitan monooleate | 15.0 | 45—55 |
| Tween 40 | Polyoxyethylene sorbitan monopalmitate | 15.7 | 41—52 |
| Tween 20 | Polyoxyethylene sorbitan monolaurate | 16.9 | 40—50 |

Dispersed phase: liquid paraffin 38.6%.
Continuous phase: distilled water 56.3%.
Emulsifying Equipment: agitator.
Emulsifier concentration: 5.1%.

Table II. Weight Ratios of Tween to Span in Emulsion Preparations

| Emulsifier | HLB | Required HLB value (%) | | | | |
|---|---|---|---|---|---|---|
| | | 10 | 11 | 12 | 13 | 14 |
| Tween 40 | 15.7 | 19.7 | 33.8 | 47.9 | 62.0 | 76.1 |
| Span 20 | 8.6 | 80.3 | 66.2 | 52.1 | 38.0 | 23.9 |
| Tween 20 | 16.9 | 16.9 | 28.9 | 41.0 | 53.0 | 65.1 |
| Span 20 | 8.6 | 83.1 | 71.1 | 59.0 | 47.0 | 34.9 |
| Tween 80 | 15.0 | 21.9 | 37.5 | 53.1 | 68.8 | 84.4 |
| Span 20 | 8.6 | 78.1 | 62.5 | 46.9 | 31.2 | 15.6 |
| Tween 20 | 16.9 | 45.2 | 53.2 | 61.1 | 69.1 | 77.0 |
| Span 80 | 4.3 | 54.8 | 46.8 | 38.9 | 30.9 | 23.0 |

**Measurement of Emulsion Stability**——Emulsion stability was measured with a measuring cylinder, Coulter counter, turbidimeter, and rheometer. These methods have already been proved useful in our previous work.⁵⁾

First, the stability of the emulsion was measured in terms of the degree of separation; the emulsion was left to stand in a glass tube at room temperature for 3 days and then the height of the drainage phase appearing in the lower part of the tube was determined as a measure of the degree of separation.

Second, the stability of the emulsion was examined in terms of the number of emulsion droplets, using the Coulter counter (model ZB, Coulter Electronics Co., Florida U.S.A.).

Third, the stability of the emulsion was evaluated in terms of the relative turbidity with a PT-201 type turbidimeter (Nihon Seimitsu Kōgaku Co., Tokyo).

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6) S. Tsukiyama, H. Takahashi, I. Takashima, and S. Hatano, *Yakugaku Zasshi*, **91**, 305 (1971).

Finally, the stability of the emulsion was evaluated in terms of its rheological properties with an RM-1 type rheometer (Shimadzu Seisakusho, Kyoto).

## Results and Discussion

### Effect of HLB Values of Blended Emulsifiers on Emulsion Stability

Both the stability of the resulting emulsions and the height of the drainage phase7) were studied in terms of the types of blended emulsifiers and the HLB value. The surfactant was a mixture of Tween and Span blended together, and the HLB values varied from 9.5 to 15.0.

Figure 1 shows the changes in the height of the drainage phase with standing time for mixtures of Tween 20 and Span 20 with five different HLB values. In spite of the presence of the emulsifier, the height of the drainage phase increased rapidly in the early stage after the preparation of the emulsion; the initial slopes became approximately constant, giving straight line plots in the range of HLB values from 12.0 to 14.0. The rate of separation of the dispersed phase increased with increase of HLB values beyond HLB=11.0. Thus, the rate of separation was greatly affected by the HLB values of emulsifiers, and it was found to decrease in the order HLB=14.0, 13.0, 12.0, 10.0, and 11.0.

The effect of HLB value on the rate of separation is shown in Fig. 2 for o/w emulsions stabilized with Tween alone and with four mixtures of Tween and Span emulsifiers. The height of the drainage phase was measured after a standing time of 1000 min after the preparation of the emulsion. It was clear that the HLB value of the emulsifier was closely related to the rate of separation. The emulsions prepared using Tween 20+Span 20 and Tween 40+Span 20 showed minimum drainage at an HLB value around 11.0. When emulsifiers such as Tween 40+Span 20, Tween 20+Span 20, and Tween 80+Span 20 were used, the height of the drainage phase increased rather sharply on the higher side of the optimum HLB, which corresponds to the most stable conditions. The rate of separation increased in the following order with blended emulsifiers: Tween 80+Span 20, Tween 20+Span 20, Tween 40+Span 20, and Tween 20+Span 80. The emulsion prepared using Tween 20+Span 80 was unstable over the whole range of HLB values studied.

Figure 3 shows the effect of HLB value on the number of droplets for o/w emulsions stabilized with Tween alone and with four mixtures of Tween and Span emulsifiers. The number of droplets, which was taken as one of the quantitative criteria of emulsion stability, was measured with the Coulter counter immediately after preparing the emulsion. The number of droplets was strongly dependent on the HLB value of the emulsifier used, and the emulsions prepared using Tween 40+Span 20, Tween 20+Span 20, and Tween 80+Span 20 showed a maximum value at an HLB value of 11.0. The number of droplets fell rather sharply on either side of the optimum HLB. However, the emulsion prepared with Tween 20 plus Span 80 did not show this tendency, and was an unstable cream. The number of

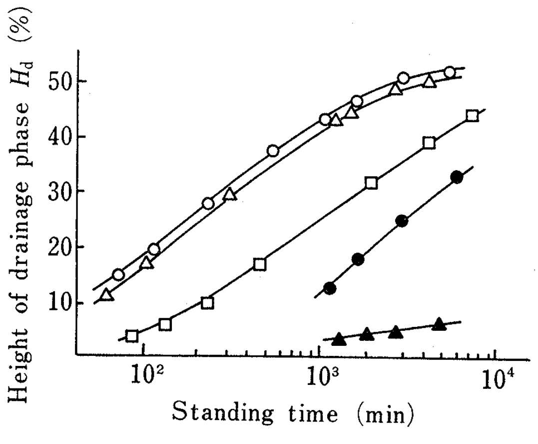

Fig. 1. Change of the Height of the Drainage Phase with Standing Time

○: HLB 14 (65: 35)*. △: HLB 13 (53: 47).
□: HLB 12 (41: 59). ▲: HLB 11 (29: 71).
●: HLB 10 (17: 83).
Dispersed phase: liquid paraffin 38.6%.
Continuous phase: distilled water 56.3%.
Emulsifier: Tween 20 and Span 20, concentration: 5.1%.
Equipment: agitator, 812 rpm.
Agitation time: 60 min.
*Weight ratio of Tween 20 to Span 20.

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7) T. Mitsui, Y. Machida, and F. Harusawa, *Am. Cosmet. and Prefum.*, **87**, 33 (1972).

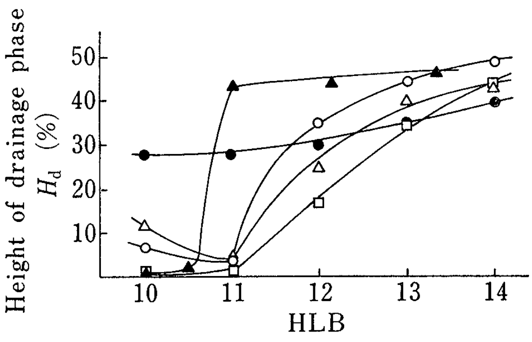

Fig. 2. Relation between the Height of the Drainage Phase and HLB Value

○: Tween 40 and Span 20 (HLB=15.7, 8.6).
△: Tween 20 and Span 20 (HLB=16.9, 8.6).
□: Tween 80 and Span 20 (HLB=15.0, 8.6).
●: Tween 20 and Span 80 (HLB=16.9, 4.3).
▲: Tween alone.
Dispersed phase: liquid paraffin 38.6%.
Continuous phase: distilled water 56.3%.
Emulsifier concentration: 5.1%.
Equipment: agitator, 812 rpm.
Agitation time: 60 min.
Standing time: 1000 min.

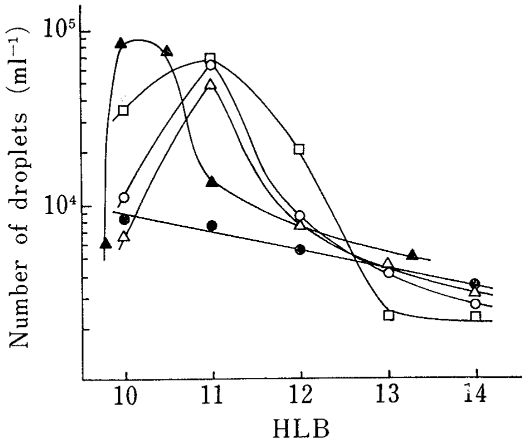

Fig. 3. Relation between the Number of Droplets and the HLB Value

○: Tween 40 and Span 20 (HLB=15.7, 8.6).
△: Tween 20 and Span 20 (HLB=16.9, 8.6).
□: Tween 80 and Span 20 (HLB=15.0, 8.6).
●: Tween 20 and Span 80 (HLB=16.9, 4.3).
▲: Tween alone.
Dispersed phase: liquid paraffin 38.6%.
Continuous phase: distilled water 56.3%.
Emulsifier concentration: 5.1%.
Equipment: agitator, 812 rpm.
Agitation time: 60 min.

droplets decreased in the following order for mixed emulsifiers: Tween 80+Span 20, Tween 40+Span 20, Tween 20+Span 20, and Tween 20+Span 80.

Figure 4 shows the effect of HLB value on the viscosity of emulsions stabilized with mixtures of Tween and Span. In this experiment, the shear rate was kept constant at 7.5 sec$^{-1}$. Logarithmic plots of the viscosity against the HLB value showed a curvilinear relationship in the range of HLB 10.0 to 14.0, which in general was consistent with the trand of the droplet number-HLB relationship at HLB values higher than 11.0. When the HLB fell below 11.0,[8] the viscosity did not decrease with decreasing HLB value, but actually increased. This may be interpreted as being due to the phase inversion phenomenon. Furthermore, the results in Fig. 4 suggest that viscous emulsions in which the rate of creaming is retarded would be produced at HLB values below the "required HLB" values. For the o/w emulsions studied, the viscosity decreased in the order Tween 40+Span 20>Tween 20+Span 20>Tween 80+Span 20>Tween 20+Span 80.

When the flow behaviors of two or more different emulsions are to be compared, their viscosities should be measured over a wide range of shear rates. The emulsions were all thixotropic, which indicates that the surfactants contribute to the stability by preventing creaming.

A typical rheogram of an emulsion prepared using a mixture of Tween 20 and Span 20 is shown in Fig. 5. The relationship of shear stress with shear rate was not linear. Accordingly, the gradient, $\Delta f/\Delta(du/dx)$, of the linear portion of the non-Newtonian flow curve was calculated and taken as the "apparent viscosity". The relationship between $\eta$ and $du/dx$ did not give a horizontal plot; $\eta$ first decreased markedly and then tended to level off with increase of $du/dx$. A hysteresis effect appeared in the emulsion prepared using Tween 20 +Span 20.

Thixotropy is formally defined as a "reversible gel-sol transition" and is caused by the build-up of a definite structure within the material. The gelled structure, upon shearing,

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[8] K.J. Lissant, "Emulsions and Emulsion Technology," Marcel Dekker Inc., New York, 1974, p. 861.

becomes a sol, and if this is allowed to remain undisturbed, it becomes gelled again. If the particles adhere to each other, but adhesion is very weak, the structure is completely destroyed at low shear rates. However, they reconstitute a gel-like state on standing, retaining enmeshed interparticle liquid.

Thixotropic system, in which agitation produces a decrease in viscosity and the original viscosity is only restored after a period of rest, show a hysteresis effect in their flow curves. The hysteresis is obtained by increasing the shear rate and then, without stopping, decreasing it. Thus, the viscosity at any particular shear rate will depend upon the amount of previous shearing it has undergone. The area bounded by the curves results from the temporary breakdown of the gel-like structure of the emulsion.

The enclosed area, termed the "hysteresis loop", is determined by the maximum shear rate and by the total shearing time. The decrease in viscosity as the emulsion is subjected to constant shearing as a function of time. If the curves form a hysteresis loop, the emulsion is thixotropic, and the area of the loop can be used as a measure of the thixotropic breakdown of the body. In general terms, the loop area may indicate the amount of structure breakdown during a shearing cycle.

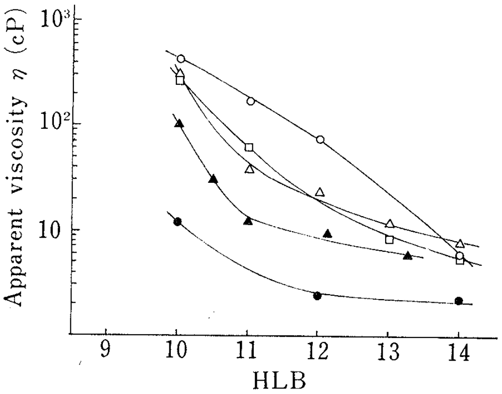

Fig. 4. Relation between the Apparent Viscosity and the HLB Value

○: Tween 40 and Span 20 (HLB=15.7, 8.6).
△: Tween 20 and Span 20 (HLB=16.9, 8.6).
□: Tween 80 and Span 20 (HLB=15.0, 8.6).
●: Tween 20 and Span 80 (HLB=16.9, 4.3).
▲: Tween alone.
Dispersed phase: liquid paraffin 38.6%.
Continuous phase: distilled water 56.3%.
Emulsifier concentration: 5.1%.
Equipment: agitator, 812 rpm.
Agitation time: 60 min.

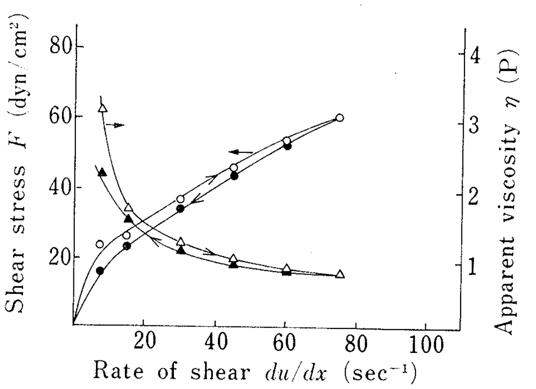

Fig. 5. Plots of Apparent Viscosity and Shear Stress against Shear Rate

○, ●: shear stress.
△, ▲: apparent viscosity.
Dispersed phase: liquid paraffin 38.6%.
Continuous phase: distilled water 56.3%.
Emulsifier: Tween 20 and Span 20, concentration: 5.1%.
Equipment: agitator, 812 rpm.
Agitation time: 60 min.
Rheometer: Shimadzu RM-1 type.

## Comparison of Emulsion Stability

Emulsion stability was considered based on the results of three measurements; (1) the height of the drainage phase, (2) the number of droplets, and (3) the viscosity of the emulsion.

First, as shown in Fig. 2, the relative height of the drainage phase in the emulsion prepared with Tween alone showed low values at HLB values below 10.5, but increased abruptly at an HLB value of 11 and then leveled off to a constant value with further increase of HLB. In general, at HLB values larger than 11.0, the drainage rate in the emulsion prepared using Tween alone was higher than that in emulsions stabilized with mixtures of Tween and Span.

Second, as shown in Fig. 3, the number of droplets reached a maximum at an HLB value of 10.0. On the other hand, the maximum appeared at an HLB value of 11.0 for emulsions stabilized with blended emulsifiers, except in the case of the mixture of Tween 20 and Span 80. The reasons for this exception will be descussed later.

Third, as shown in Fig. 4, the viscosity curve of the emulsion prepared using Tween alone had a shape similar to those obtained with emulsions stabilized with blended emulsifiers. The viscosity of the emulsion prepared using Tween alone was clearly lower than those of the emulsions stabilized with blended emulsifiers, except in the case of the mixture of Tween 20 and Span 80. The creamy emulsion formed by the use of Tween alone had a much softer texture than those stabilized with blended emulsifiers.

### Molecular Association Mechanism at the Oil-Water Interface

Molecular association at an oil-water interface between Tween and Span molecules may be fairly specific. Span 20 molecules, for example, will be oriented so that the hydrocarbon chain (which contains 11 carbon atoms) lies on the oil side of the interface and the sorbitan ring lies on the aqueous side. The hydrocarbon chains of the oriented Span 20 molecules are prevented from moving close together by the width of the sorbitan rings. On the other hand, in the case of Tween 40 molecules, because of the strong hydrophilicity exhibited by the polyoxyethylene chains, the molecules are oriented at the oil-water interface in such a way that only a part of each hydrocarbon chain lies within the oil phase, the other part being located in the water phase on the other side of the interface. When Span 20 and Tween 40 are used together, those parts of the Tween 40 hydrocarbon chains that are located in the oil phase penetrate between the adsorbed Span 20 molecules. The distance between adjacent hydrocarbon chains is thereby reduced, so that the probability of attraction between them increases and the van der Waals force[9] become significant.

The narrow column of continuous phase between flattened droplet surfaces is stabilized by the hydrated polyoxyethylene chains of the Tween 40 molecules. Each Tween 40 molecule has three such chains, and they may interweave to provide a gel-like structure. This structure provides a good stability against droplet coalescence, and an additional stabilization is provided by the closely packed hydrocarbon chains of alternating Span 20 and Tween 40 molecules on the oil side of the interface.

As mentioned above, stable emulsions were formed when a condensed film was formed from two components, one oil-soluble and the other water-soluble. These two molecular species exhibit affinity for each other, both being held at the interface and oriented with the polar groups in the water and the hydrocarbon groups in the oil phase. Such a film exhibits strong lateral attraction between the molecules and forms an effective barrier against coalescence of the dispersed phase.

On the other hand, the emulsion prepared using a mixture of Tween 20 and Span 80 showed no minimum in the drainage rate at an HLB value of 11.0 and was unstable over the whole range of HLB. The reason for this will be discussed below.

Nonionic Span 80 is a strongly lipophilic and poorly hydrophilic compound, and has a low HLB value of 4.3. In contrast, the long polyoxyethylene chains of Tween 20 are strongly hydrophilic, and this surfactant has a very high HLB value of 16.9. In general, emulsifiers with low HLB values are known to promote the formation of water-in-oil emulsions while those with high HLB values tend to produce oil-in-water emulsions. Accordingly, the emulsion prepared using the mixture of Span 80 and Tween 20 is presumably unstable because of the very large difference in HLB values (12.6) between Span 80 and Tween 20. In contrast, the emulsion prepared using a mixture of Span 20 and Tween 80 or Span 20 and Tween 40 is stable because the difference of HLB values is only 6.4 or 7.1. Thus, it appears that the difference of HLB values between Span and Tween should lie within a moderate range if a stable emulsion is to be obtained.

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9) J. Boyd, C. Parkinson, and P. Sherman, *J. Colloid Interface Sci.*, **41**, 359 (1972).