Span and Tween

Sorbitan esters and their ethoxylates

Croda's unique expertise in ester technology and continuing commitment to customers has established the company as a world-leader in the supply of sorbitan esters and derivatives for an array of applications. A unique understanding of the highly complex properties and functions of sorbitan esters has been developed to ensure customer developments are cutting edge in today's highly competitive environment.

The Spans and Tweens are a range of mild nonionic surfactants providing formulating benefits in a number of Home Care applications. Croda's Span and Tween materials have long-standing food and pharmacopoeia approval with a safe history of use.

As nonionics, Spans and Tweens offer many advantages over ionic surfactants including increased stability, formulating flexibility and wider compatibility. They are stable in mild acids, alkalis and electrolytes and do not react with ionic ingredients or actives. By combining Spans and Tweens at different ratios, formulators are able to produce systems with a wide HLB range to emulsify most oils and waxes. Certain Spans and Tweens are also highly effective solubilisers, dispersing agents and wetting aids.

Functional benefits

- Nonionic emulsifiers and co-emulsifiers
- Solubilisers
- Dispersants
- Wetting agents
- Stable over a wide pH range
- Electrolyte tolerant

Span – Sorbitan esters

Croda's sorbitan esters are marketed under the Span product name and are produced by the dehydration of sorbitol. Esterification with fatty acids in a controlled chemical process gives reproducible materials at the quality expected from Croda. A monoester of a generic Span can be represented as:

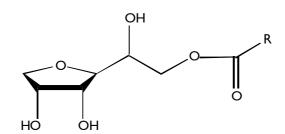


Figure 1: Chemical structure – Sorbitan monoester

R is the alkyl group of the fatty acid. Further esterification with fatty acids results in polyesters. The sesqui and triesters contain 1-2 and 3 fatty acid groups respectively. The HLB value of the range decreases with increasing degree of esterification, conferring superior solubility in lipophilic materials.

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Tween – Polyethoxylated sorbitan esters

In simple terms, Tweens are ethoxylated Spans. A polyethoxylated monoester of 3,6-sorbitan can be represented as:

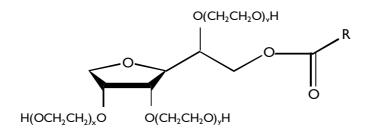


Figure 2: Chemical structure - polyethoxylated monoester

R is the alkyl group of a fatty acid and (x+y+z) is the total number of moles of ethylene oxide.

Tweens are hydrophilic in nature and are soluble or dispersible in water and dilute solutions of electrolytes. The solubility of Tweens in aqueous solutions increases with the degree of ethoxylation. For a fixed degree of ethoxylation, aqueous solubility decreases as the number of ester groupings increases. For a fixed degree of ethoxylation and esterification, aqueous solubility decreases as the molecular weight of the fatty acid increases.

Product Range

Product Name	Chemical Identity	Product Name	Chemical Identity
Span 20	Sorbitan monolaurate	Tween 20	PEG-20 sorbitan monolaurate
Span 40	Sorbitan monopalmitate	Tween 21	PEG-4 sorbitan monolaurate
Span 60	Sorbitan monostearate	Tween 40	PEG-20 sorbitan monopalmitate
Span 80	Sorbitan monooleate	Tween 60	PEG-20 sorbitan monostearate
Span 83	Sorbitan sesquioleate	Tween 61	PEG-4 sorbitan monostearate
Span 85	Sorbitan trioleate	Tween 65	PEG-20 sorbitan tristearate
Span 120	Sorbitan isostearate	Tween 80	PEG-20 sorbitan monooleate

RODA



Solubility

Table 1 below provides information on the solubility of the Span and Tween range at 10% w/w in a number of common solvents and oils at 25°C.

Product Name	Water	Mineral Oil	Kerosene	Rapeseed oil	Methyl oleate	Butyle stearate
Span 20	PS	S	S	PS	S	S
Span 40	PS	G				
Span 60	PS	G	I			I
Span 80	PS	S	S	S	PS	PS
Span 83	PS	S	PS	S	PS	PS
Span 85	PS	S	S	S	S	S
Span 120	PS	S	PS	S	PS	PS

Product Name	Water	Mineral Oil	Kerosene	Rapeseed oil	Methyl oleate	Butyle stearate
Tween 20	PS					I
Tween 40	S					
Tween 60	PS		I	PS		I
Tween 65	G	PS	PS		S	I
Tween 80	S			PS	PS	

 Key
 S – soluble
 PS – partly soluble
 G – gel formed
 I – insoluble

 Table 1: Solubility Data

Emulsification

Table 2 indicates the quality of oil in water emulsions produced at 25°C when water (90 parts by weight) is added under stirring to the solvent or oil (10 parts by weight) containing 10% w/w Tween (i.e. final surfactant concentration in the test system is 1% w/w).

Product Name	Mineral Oil	Kerosene	Rapeseed oil	Methyl oleate	Butyle stearate
Tween 20	Ν	Р	F	G	F
Tween 40	Р	F	F	G	F
Tween 60	Р	F	F	G	F
Tween 65	G	G	F	G	F
Tween 80	Р	Р	F	G	F

KeyG – Good emulsionF – FairP – PoorN - NegligibleTable 2: Emulsification data

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Spans based on unsaturated or branched chain fatty acids act as effective water in oil emulsifiers. When combined with the corresponding Tween, Spans are efficient coemulsifiers for oil in water systems. Table 3 details the approximate HLB (hydrophilic-lipophilic balance) of each member of the Span / Tween range. By adjusting the Span to Tween ratio, various HLB values can be achieved allowing the emulsification of many industrial raw materials.

Product Name	HLB Value	Product Name	HLB Value	
Span 20	8.6	Tween 20	16.7	
Span 40	6.7	Tween 21	13.3	
Span 60	4.7	Tween 40	15.6	
Span 80	4.3	Tween 60	14.9	
Span 83	3.7	Tween 61	9.6	
Span 85	1.8	Tween 65	10.5	
Span 120	4.7	Tween 80	15.0	

Table 3: HLB values of the Span and Tween range

Formulating guidelines for emulsion systems

According to well established emulsification principles a combination of a high and low HLB emulsifier is often more effective then the use of a single emulsifier. Combinations of Span and Tween products can therefore be used to develop stable oil in water emulsions of various materials.

Through experimentation it is important to establish the required HLB of the material to be emulsified and the appropriate chemical type of the emulsifier blend. Selection of the appropriate chemistry is as important as choosing the correct HLB. For example, emulsifiers with an unsaturated alkly chain, such as an oleyl chain, have an increased affinity for oils with unsaturated bonds. In this case a blend of Span 80 and Tween 80 would be recommended to emulsify an oil like rapeseed oil. Similarly, a blend of emulsifiers with saturated alkyl chains such as Span 60 and Tween 60 would be appropriate for the emulsification of these saturated materials.

Most raw materials that are likely to be emulsified have a required HLB value, e.g. paraffinic mineral oil has a required HLB value of 10. In order to develop a stable emulsion of this raw material a blend of Span 80 and Tween 80 combined to give a HLB value of 10 could be evaluated at different concentrations. Further minor adjustments may be required to allow for variations in individual grades of oils.

In order to calculate how much of emulsifier (A) to blend with emulsifier (B) to attain a given HLB value of X, the following equation can be utilised:

% (A) =
$$\frac{(X - HLB_B) \times 100}{HLB_A - HLB_B}$$

% (B) = 100 - % (A)



To calculate the blend of Span 80 and Tween 80 to given a HLB value of 10 can be realised as shown below:

% Tween 80 =
$$\frac{(10 - 4.3) \times 100}{(15 - 4.3)} = 53.3\%$$

% Span 80 = 100 - 53.3 = 46.7%

If the required HLB of the material (or blend of materials) to be emulsified is not known this can be determind by experimenting. Evaluation of the stability of emulsions formed with blends of an appropriate Span and Tween pair covering a range of HLB values will identify the required HLB.

The optimum concentration of the emulsifier blend can then be determined by experimentation. Generally 10% of the level of the emulsified material is a useful starting point, i.e. to make a 30% emulsion of oil would usually require an optimum level of 3% emulsifier blend.

Product applications

Span and Tween surfactants find widespread use in a diverse range of household consumer products and are useful as emulsifers, solubilisers, wetting agents and dispersants.

Polishes

Spans and Tweens are key emulsifying agents for a number of applications. By using combinations of Spans with their corresponding Tweens it is possible to prepare a variety of oil in water and water in oil emulsion systems. Span 80 is excellent for water in oil emulsification of hydrocarbons and is particularly useful in aerosol systems such as multisurface spray polishes and cleaners. Water in oil based aerosol polishes using Span 80 break down rapidly on spraying ensuring an even application of wax and silicone. Span 60 and Span 80 when used in combination with Tween 60 and Tween 80 are excellent emulsifying systems for silicone fluids in furniture polishes, shoe polishes and vehicle exterior and interior polishes.

Air Care

Tweens are extremely versatile as solubilisers for all types of fragrances and perfumes used in air fresheners and other household products. Tween 20 and Tween 80 have high HLB values and are of particular interest when solubilising volatile components. Tween 20, a fully saturated ester, is most commonly used in this application due to its low odour. Typical inclusion levels are 1:1 Tween to fragrance, depending on the formulations and fragrance to be solubilised. Tweens are recommended for odour neutralisers and solvent based degreasers.

Wipes

For quick and easy removal of oily stains, Tweens can be incorporated into wipe formulations and added to non-woven substrates. Tween 20, 80 and 85 are helpful in creating on action emulsions with oily fats helping cleaning efficiency. Tween 20 has the additional benefit of being a mildness additive and is suitable for use in wet wipes where contact with the wipe may be prolonged.

CRODA

Hand Barrier Creams

Heavy duty hand cleaners are used for easy removal of oils, dirt and greases. Tween 21 and 60 may be used to form microemulsion gels based on solvents such as odourless kerosene or as a green alternative, Prifer 6813 Croda's ecofriendly low odour degreasing solvent. Barrier products form a film which is designed to protect the skin from the effects of oil and water borne irritants. Combinations of Span 60 and Tween 60 or Span 80 and Tween 80 are good based emulsifying systems which can be tailored to produce either oil or water resistant products. They are suitable for vegetable oils and lanolin derivatives. Tween 80 in particular is a useful emulsifier for oil-resistant barrier products based on hydrophilic film-formers such as methyl cellulose of gum Arabic.

Formulations

Reference Number	Name	Product
HC/FC/02	Furniture cream with silicone	Span 80, Tween 80
HC/FC/10	Trigger pack furniture / multisurface polish	Span 85, Tween 85
HC/AC/05	Car overbody wax emulsion	Span 80, Tween 80
HC/AF/01	Aerosol air freshener	Span 80
HC/FC/19	Creamy liquid shoe wax	Tween 85
HC/SC/04	Barrier Lotion	Span 60, Tween 60

Biodegradability

Spans are considered to be readily biodegradable and would not be expected to persist indefinitely in the environment. Tweens are considered to be inherently biodegradable and would not be expected to persist indefinitely in the environment.

Health and safety

Spans and Tweens are well established raw materials used in a variety of applications. Health and safety data handling advice on individual products is provided on separate material safety data sheets that can be provided upon request.

Non-warranty

The information in this publication is believed to be accurate and is given in good faith, but no representation or warranty as to its completeness or accuracy is made. Suggestions for uses or applications are only opinions. Users are responsible for determining the suitability of these products for their own particular purpose. No representation or warranty, expressed or implied, is made with respect to information or products including, without limitation, warranties of merchantability, fitness for a particular purpose, non-infringement of any third party patent or other intellectual property rights including, without limit, copyright, trademark and designs. Any trademarks identified herein are trademarks of the Croda group of companies.

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