

Crills and Crillets

Sorbitan esters and their ethoxylates

Crills and Crillets are a range of mild nonionic surfactants providing formulating benefits in a number of personal care applications. Entirely vegetable-derived, Croda's Crills and Crillets have long-standing food and pharmacopoeia approvals and a safe history of use in cosmetic products.

As nonionics Crills and Crillets offer many advantages over ionic surfactants such as soaps, including increased stability, formulating flexibility and wider compatibility. They are stable to mild acids, alkalis and electrolytes and do not react with ionic ingredients or actives. By combining Crills and Crillets at different ratios, formulators are able to produce systems with a wide HLB range to emulsify most cosmetic oils and waxes. Certain Crills and Crillets are additionally 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
- Compatible with a wide range of cosmetic actives eg AHA/BHA, cationics, nonionics

Applications

- O/W and W/O creams and lotions
- Sun protection and tanning products
- Antiperspirants and deodorants
- Depilatories
- Hair dyes
- Colour cosmetics
- Bath and massage oils
- EDT, aftershaves and colognes

Product range

Product name	INCI name	Pharmacopoeia monograph
Crill 1	Sorbitan Laurate	EP, NF
Crill 2	Sorbitan Palmitate	EP, NF
Crill 3	Sorbitan Stearate	EP, NF
Crill 4	Sorbitan Oleate	EP, NF
Crill 43	Sorbitan Sesquioleate	NF
Crill 45	Sorbitan Trioleate	EP, NF
Crill 6	Sorbitan Isostearate	-
Crillet 1 Super	Polysorbate 20	EP, NF
Crillet 2 Super	Polysorbate 40	NF
Crillet 3 Super	Polysorbate 60	EP, NF
Crillet 4 Super	Polysorbate 80	EP, NF
Crillet 45	Polysorbate 85	-

Crills - sorbitan esters

Crills are partial esters of natural fatty acids and sorbitan, the cyclic ether produced by the dehydration of the hexahydric alcohol, sorbitol. A monoester can be represented by the following general formula where 'R' is the alkyl group of the fatty acid.

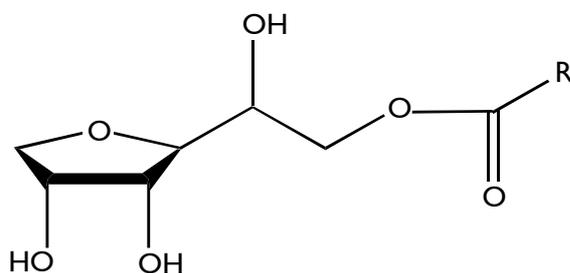


Figure 1 Chemical structure - monoester

Properties and functions

Crill 4, 43, 45 and 6 used alone act as effective water in oil (W/O) emulsifiers. When combined with the corresponding Crillet, Crills are efficient coemulsifiers for oil in water (O/W) systems. Manipulation of the Crill/Crillet ratio produces emulsifying systems of various HLB (hydrophilic-lipophilic balance) values, allowing the emulsification of many cosmetic oils and waxes. Specific properties and functions are detailed below.

Product name	Description	HLB	Properties and functions
Crill 1	Pale yellow liquid	8.6	Most hydrophilic of the Crill range, soluble in many fatty compositions and solvents. Acts as a coemulsifier in O/W emulsions, often used in combination with Crillet 1, although other Crillets may be employed
Crill 2	Cream solid	6.7	Possesses a wax-like structure which is useful where rigidity is needed in lipophilic compositions
Crill 3	Cream/yellow solid	4.7	Produces stable O/W emulsions with good aesthetics when combined with its polyethoxylated derivative, Crillet 3. Recommended for the emulsification of fatty alcohols, esters, mineral and silicone oils. Ideal for skin creams and lotions
Crill 4	Amber liquid	4.3	Liquid W/O emulsifiers, particularly recommended for unsaturated lipid components such as oleyl alcohol or vegetable oils. May also be used with the corresponding Crillet in O/W emulsions. Dispersing agents for insoluble liquids in other lipophilic liquids. Crill 4 and 43 are used as wetting agents and dispersants for pigments in colour cosmetics and zinc oxide/titanium dioxide in suncare products
Crill 43	Amber viscous liquid	3.7	
Crill 45	Amber liquid	1.8	
Crill 6	Yellow liquid	4.7	Excellent W/O emulsifier for protective, baby care and general purpose emollient creams. Wetting and dispersing agent for physical sunscreens and decorative cosmetics. Based on isostearic acid, a completely saturated branched chain ester, Crill 6 is not prone to oxidation and associated changes in colour or odour. Low setting point makes it useful in pourable products

Crillets - Polyethoxylated sorbitan esters

Crillets are polyethoxylated partial esters of sorbitol, sorbitans and isosorbide. A polyethoxylated monoester of 3,6-sorbitan is represented in figure 2 where 'R' is the alkyl group of a fatty acid and (x+y+z) is the total number of moles of ethylene oxide.

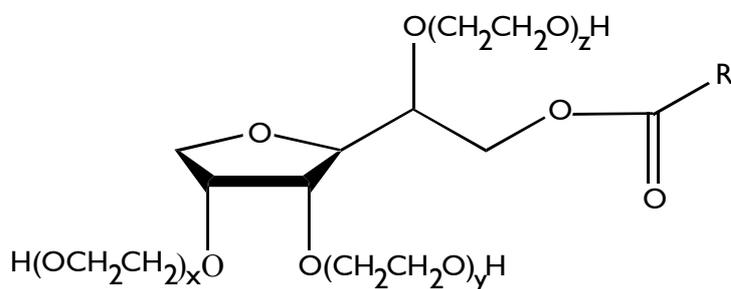


Figure 2 Chemical structure - polyethoxylated monoester

Properties and functions

Crillets (Polysorbates) are excellent O/W emulsifiers, solubilisers, wetting agents and dispersants. In emulsion systems they are commonly used in combination with the corresponding Crill. Manipulation of the Crill/Crillet ratio produces emulsifying systems of various HLB (hydrophilic-lipophilic balance) values, allowing the emulsification of many cosmetic ingredients. Specific properties and functions are detailed below.

Product name	Description	HLB	Properties and functions
Crillet 1 Super	Clear yellow liquid	16.7	Fully saturated liquid ester, recommended as an emulsifier for O/W systems and effective solubiliser for essential oils and perfumes in aqueous and aqueous/alcoholic systems. Also used as a mildness additive in detergent systems eg baby shampoo and cleansing agent in wet wipes
Crillet 2 Super	Yellow pasty liquid	15.6	Co-solvent and wetting agent
Crillet 3 Super	Yellow liquid/soft solid	14.9	Produces stable O/W emulsions, especially when combined with Crill 3 and cetostearyl alcohol or other fatty alcohols. Excellent for the emulsification of esters, mineral and silicone oils. Skin creams exhibit good sensory profile
Crillet 4 Super	Clear yellow liquid	15.0	O/W emulsifier and dispersant often used in conjunction with the appropriate Crill. Good solubilising properties, recommended in systems with unsaturated lipid components such as oleyl alcohol and vegetable triglycerides
Crillet 45	Amber liquid	11.0	Less hydrophilic than Crillet 4. Excellent dispersing agent for vegetable oils, particularly useful in bath and massage oils

Key applications

Oil in water emulsions

For the formulation of stable, cost effective O/W emulsions a combination of Crill 3 and Crillet 3 is particularly recommended. The ratio of each emulsifier can be adjusted to match the required HLB of a wide range of oil phase ingredients. Crill 3 and Crillet 3 can be used for emulsifying a number of esters, mineral and silicone oils. This emulsifying system can be used to formulate thin lotions or thick creams by adjusting the level of fatty alcohol present or by the use of water phase thickeners. Formulating guidelines for basic systems are provided overleaf.

Combinations of Crill/Crillet 1 or 4 can be used in the same way; a Crill/Crillet 4 emulsifying system is particularly recommended for unsaturated vegetable oils.

Typical O/W cosmetic products include moisturising face creams and lotions, body lotions and hand creams, aftersuns and cleansing lotions.

Water in oil emulsions

Crill 6 and Crill 4 are particularly recommended as emulsifiers for W/O systems. Both materials are based upon branched or unsaturated lipophiles and are liquid at room temperature. Crill 6 is often used as the sole emulsifier for W/O creams and lotions, particularly where the external phase is mineral oil. Its low setting point is useful when formulating emulsions which must remain free from sedimentation and crystallisation.

W/O emulsions are commonly used when formulating protective skin creams, night and cold creams and baby creams.

Pigmented systems

Crill 6 and Crill 4 are recommended as dispersing agents when introducing physical sunscreens and pigments into oily vehicles. Using a dispersing agent results in a more uniform dispersion and slows agglomeration of particulate materials to give improved emulsion stability. Applications include sunscreens, colour cosmetics and protective baby creams and lotions.

Aqueous and aqueous/alcoholic systems

Crillet 1 is an excellent solubiliser for fragrance oils, oil soluble vitamins and essential oils. It is a useful ingredient in aqueous systems such as hair gels and spritzes and can help reduce the levels of alcohol required to solubilise fragrances in aqueous/alcoholic products eg EDT and aftershaves.

Detergent systems

Crillet 1 is widely known to function as a mildness additive in detergent systems and is frequently used to formulate gentle baby shampoos.

Formulating guidelines for emulsion systems

It is well established that a combination of a high and a low HLB emulsifier is often more effective than the use of a single emulsifier. Combinations of Crills and Crillets 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 alkyl chain, such as an oleyl chain, have an increased affinity for oils with unsaturated bonds. In this case a blend of Crill 4 (Sorbitan Oleate) and Crillet 4 (Polysorbate 80) would be recommended to emulsify vegetable oils. Similarly a blend of emulsifiers with saturated alkyl chains, for example Crill 3 (Sorbitan Stearate) and Crillet 3 (Polysorbate 60), would be appropriate for the emulsification of saturated materials.

Most raw materials that are likely to be emulsified (eg mineral and vegetable oils, emollient esters, silicone oils) have a published required HLB value. For example, required HLB values of approximately 10 are usually quoted for mineral oils. In order to develop a stable emulsion of mineral oil, a blend of Crill 3 (Sorbitan Stearate) and Crillet 3 (Polysorbate 60), combined to give an HLB value of 10, could be evaluated at different concentrations. Further minor adjustments will be required to optimise formulation stability, viscosity, aesthetics etc.

In order to calculate how much of emulsifier (A) to blend with emulsifier (B) to reach a given required HLB of X:

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

$$\% (B) = 100 - \% (A)$$

To calculate the blend of Crill 3 (Sorbitan Stearate) and Crillet 3 (Polysorbate 60) to emulsify an oil with a required HLB of 10:

HLB of Crillet 3 = 14.9

HLB of Crill 3 = 4.7

$$\% \text{ Crillet 3} = \frac{100 (10 - 4.7)}{(15 - 4.7)} = 51.5\%$$

$$\% \text{ Crill 3} = 100 - 51.5 = 48.5\%$$

If the required HLB of the material or blend of materials to be emulsified is not known, this can be determined by experimentation. Evaluation of the stability of emulsions formed with blends of an appropriate Crill and Crillet pair covering a range of HLB values will identify the required HLB.

The optimum concentration of the emulsifier blend can then be determined by experiment. Generally 10-20% of the level of the emulsified material is a useful starting point, ie to make a 30% emulsion of oil would usually require an optimum level of 3% emulsifier blend. Both emulsifiers are usually introduced into the oil phase.

Solubility

Table 1 provides data on the solubility of the Crill and Crillet range at 10% w/w in a number of common solvents and oils at 25°C.

Product	Caprylic/ capric triglyceride	Soya bean oil	Ethyl oleate	Isopropyl myristate	Mineral oil	Glycerin	Water
Crill 1	PS	PS	PS	PS	S	I	I
Crill 2	PS	PS	I	I	G	I	I
Crill 3	PS	PS	PS	PS	G	I	I
Crill 4	PS	S	PS	PS	S	I	I
Crill 43	PS	S	PS	PS	S	PS	I
Crill 45	S	S	S	S	S	PS	I
Crill 6	PS	S	PS	PS	S	I	I
Crillet 1 Super	PS	S	PS	PS	PS	S	S
Crillet 2 Super	PS	PS	I	I	I	I	S
Crillet 3 Super	PS	I	PS	I	I	G	PS
Crillet 4 Super	PS	PS	I	I	I	I	S
Crillet 45	PS	PS	S	S	I	I	PS

Key S - Soluble PS - Partially soluble G - Gel formed I - Insoluble

Table 1 Solubility data of Crill and Crillet range

Specifications

Detailed selling specifications for individual products are available on request.

Biodegradability

The Crills are considered to be readily biodegradable and would not be expected to persist indefinitely in the environment. The Crillets are considered to be inherently biodegradable and would not be expected to persist indefinitely in the environment.

Health and safety

The Crills and Crillets are well-established raw materials used in a variety of applications. Certain sorbitan esters are accepted as food additives in Europe. Sorbitan esters are included in the FDA Inactive Ingredients guide. Polysorbates 60 and 80 are GRAS listed. Polysorbates 20, 40, 60 and 80 are accepted as food additives in Europe and are included in the FDA Inactive Ingredients guide. Health and safety data and handling advice on individual products is provided on separate material safety data sheets, available on request.

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