PharmacoLearn

MPH204T Cosmetic and Cosmeceuticals, M.Pharm Semester 2

Unit 3: Formulation Building Blocks

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3.1 The building block idea

A cosmetic formulation is assembled from functional classes of ingredients, and this unit teaches the classes before the products. Every cream, shampoo or toothpaste in this unit is a short list of decisions: a **surfactant** system to cleanse or to emulsify, **emollients** to give the skin feel and barrier support, **rheology additives** to give the product its body and keep it suspended and stable, **emulsifiers** holding oil and water together, **preservatives** keeping it microbiologically safe through its shelf life and use, and the finishing classes, humectants, fragrance, colour, chelating agents, antioxidants and pH adjusters. Read the five named products of this unit (moisturizing cream, vanishing cream, cold cream, shampoo, toothpaste) as five arrangements of the same blocks; the differences between them are which blocks dominate. This block thinking is what the examination tests: given a product, name the blocks and the example ingredients; given a block, state its classes, examples and failure modes.

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Assembling a cosmetic from building blocks
Water phase: water, humectants, water soluble actives
   +
Oil phase: emollients, emulsifiers, oil soluble actives
   |
   v
Emulsify and cool with mixing
   |
   v
Rheology adjustment to target body and stability
   |
   v
Preservative, fragrance, colour, pH adjustment
   |
   v
Fill, with microbiological and stability testing
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3.2 Surfactants: classification by charge

Surfactants (surface active agents) are molecules with a water loving head and an oil loving tail, which is why they gather at interfaces, lower surface and interfacial tension, wet surfaces, solubilise oils into micelles, foam, and stabilise emulsions. They are classified by the charge of the head group in solution, and the classification predicts properties well enough to organise the whole field.

Class	Head charge	Representative examples	Properties and cosmetic applications
Anionic	Negative	Sodium lauryl sulfate, sodium laureth sulfate, sodium cocoyl isethionate, soap (sodium stearate)	Strong cleansing and foaming, the primary detergents of shampoos, toothpastes and cleansers; the stronger members irritate skin and eyes
Cationic	Positive	Cetrimonium chloride, behentrimonium chloride, benzalkonium chloride	Substantive to negatively charged hair and skin, so the conditioning agents of hair conditioners and rinses; poor detergents; some are antimicrobial
Nonionic	Uncharged	Polysorbates, sorbitan esters, cetearyl alcohol ethoxylates, cocamide DEA, alkyl polyglucosides	Mild, stable across pH, low foam alone; the emulsifiers and solubilisers of creams and lotions, and foam boosters and thickeners with anionics

Class	Head charge	Representative examples	Properties and cosmetic applications
Amphoteric (zwitterionic)	Both, pH dependent	Cocamidopropyl betaine, coco amphoacetate	Mild co surfactants that reduce the irritation of anionics, boost and stabilise foam; standard in baby and facial products

Two working concepts complete the picture. Above the **critical micelle concentration**, surfactant molecules aggregate into micelles with tails inward, and it is micellar solubilisation of sebum and oily soil that does most cleansing work. The **hydrophile lipophile balance (HLB)** scale grades emulsifiers by their water versus oil affinity, low HLB suiting water in oil emulsions and high HLB oil in water emulsions, and blends are chosen to match the required HLB of the oil phase.

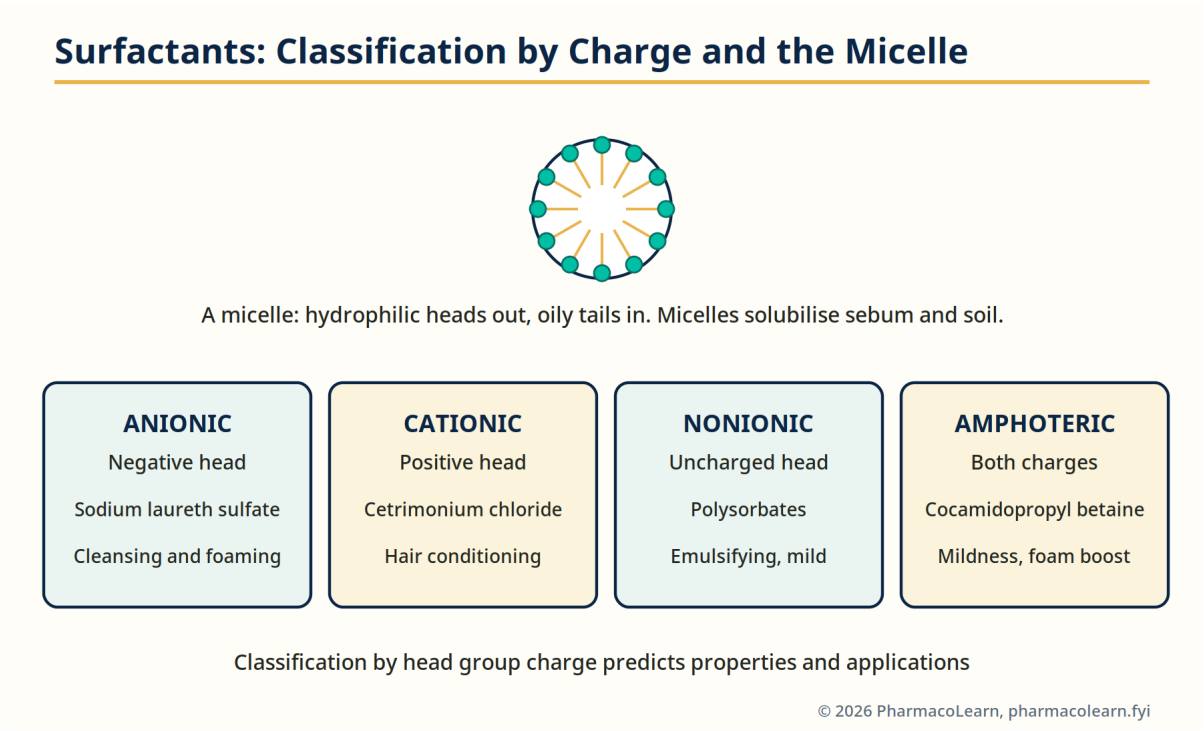

Figure: A micelle and the four surfactant classes. Head group charge predicts cleansing power, mildness and application.

3.3 Surfactants: applications in cosmetic products

Applications follow from the table. In shampoos, an anionic primary surfactant (commonly sodium laureth sulfate) does the cleaning, an amphoteric such as cocamidopropyl betaine cuts irritation and builds foam quality, and a nonionic or polymeric thickener sets viscosity. In skin cleansers and face washes the same architecture is diluted and softened, with milder anionics such as sodium cocoyl isethionate. In toothpaste, sodium lauryl sulfate provides foam and helps disperse the paste, at levels balanced against mucosal irritation. In creams and lotions, nonionic emulsifier pairs do the surfactant work of holding the emulsion together rather than cleansing. Cationic surfactants earn their place after washing, in conditioners, where their positive charge deposits them on the damaged, negatively charged sites of the hair shaft, reducing combing friction and static. The formulation skill is matching charge, mildness and secondary function to the product's site from Unit 2: what is an excellent shampoo anion is an unacceptable eyelid cleanser.

3.4 Emollients: classification and application

Emollients are the ingredients that soften and smooth skin and hair and give a product its sensory signature. Applied to skin they spread over the stratum corneum, fill the spaces between shedding corneocytes, reduce the scaly feel of dryness and partly occlude the surface, so they are both a feel

ingredient and a mild barrier ingredient. They are classified by origin and chemistry, and graded in practice by spreadability and after feel, from dry, fast spreading esters to heavy, greasy butters.

Class	Examples	Character and typical use
Hydrocarbons	Mineral oil, petrolatum (petroleum jelly), squalane	Inert, stable, strongly occlusive; petrolatum is the most effective single reducer of TEWL; bases of cold creams and ointment like products
Fatty esters	Isopropyl myristate, cetyl palmitate, caprylic/capric triglyceride	The great feel adjusters, light to medium spread, reduce the greasiness of hydrocarbon bases
Fatty alcohols and acids	Cetyl alcohol, stearyl alcohol, stearic acid	Body and structure in creams, co emulsifiers, the backbone of vanishing cream
Natural oils and butters	Coconut oil, almond oil, shea butter, cocoa butter	Traditional and herbal positioning (Unit 5), nourishing feel, variable oxidative stability
Silicones	Dimethicone, cyclomethicone	Exceptional spreading and a dry, silky after feel, volatile grades evaporate without residue; common in modern creams and hair serums
Lanolin and derivatives	Lanolin, lanolin alcohols	Wool wax resembling skin lipids, excellent emolliency and water absorption, occasional sensitization

Emollient choice is product definition: the vanishing cream of section 3.9 feels dry because its emollient is largely stearic acid that crystallises on the skin, while the cold cream feels rich because it is built on mineral oil and wax.

3.5 Rheological additives: classification and application

Rheology additives control how a product flows, its viscosity, body, suspension stability and pickup. A shampoo must pour but not run off the hand; a cream must hold a peak in the jar yet spread to nothing; a toothpaste must stand on the brush and then break down in the mouth. The classes:

- **Natural gums:** xanthan gum, guar gum and its cationic derivative guar hydroxypropyltrimonium chloride (also a hair conditioner), cellulose gums such as carboxymethylcellulose and hydroxyethylcellulose. Water swelling polymers giving body at low use levels, broadly compatible, subject to microbial attack and so needing preservation.
- **Clays and mineral thickeners:** bentonite and hectorite, plate like minerals that build thixotropic gels, suspending powders in calamine type lotions and face packs; magnesium aluminium silicate is the cosmetic grade workhorse.
- **Synthetic polymers:** the carbomers, crosslinked acrylic acid polymers neutralised in use to give clear, high yield value gels at fractions of a percent, the standard thickener of gels and modern creams; acrylate copolymer emulsion thickeners for lotions.
- **Waxes and fatty structuring agents:** beeswax, carnauba and candelilla waxes and cetyl and stearyl alcohols, which thicken by building a crystal network in the oil phase, essential in sticks, balms and cold creams.
- **Inorganic salts and surfactant structuring:** sodium chloride thickens anionic shampoo systems by shrinking micelles into rods, the cheapest rheology control in the subject; alkanolamides historically did similar work.

The governing practical concepts are yield value (stress needed to start flow, which keeps particles and droplets suspended), thixotropy (viscosity falling under shear and recovering at rest, the behaviour of a good cream) and the danger of over thickening, which traps air, slows manufacture and ruins spreadability.

3.6 Antimicrobial preservatives: merits and demerits

Any water containing cosmetic is a nutrient medium, and a preservative system is a safety requirement, not an option: contamination of eye area and baby products with organisms such as Pseudomonas aeruginosa has caused serious infections, which is why preservation is regulated and challenge tested. The principal classes, with their honest merits and demerits:

Class	Examples	Merits	Demerits
Parabens	Methylparaben, propylparaben	Broad spectrum, cheap, stable, effective at low levels over a wide pH range, decades of use data	Public controversy (section 3.13), restricted for some members and uses in the EU, weak against some fungi alone
Formaldehyde liberators	DMDM hydantoin, imidazolidinyl urea, quaternium-15	Very effective, especially against bacteria including Pseudomonas	Release formaldehyde, a known sensitizer; controversial (section 3.13)
Isothiazolinones	Methylisothiazolinone, methylchloroisothiazolinone blend	Potent at very low levels, broad spectrum	Strong sensitizers; heavily restricted in the EU, leave on use largely prohibited there
Organic acids	Benzoic acid, sorbic acid, dehydroacetic acid	Food grade familiarity, good consumer acceptance	Active only in the undissociated form, so effective only at acid pH; weaker against bacteria
Alcohols and glycols	Phenoxyethanol, chlorphenesin, caprylyl glycol	Phenoxyethanol is the modern workhorse, broad, stable, good tolerance; glycols boost other preservatives	Phenoxyethanol weaker against fungi, used with boosters; high alcohol systems sting and dry
Others	Chlorhexidine, triclosan (historically), benzalkonium chloride	Specific niches: antiseptic and oral products, cationic preservation	Triclosan restricted over environmental and resistance concerns; cationics inactivated by anionics

The professional answer to "which preservative" is always a system: a primary antimicrobial, a chelator such as disodium EDTA that weakens bacterial membranes, a glycol booster, hygienic manufacture, and packaging that limits recontamination, verified by a preservative efficacy (challenge) test in which the product is inoculated with standard organisms and must reduce their counts to the pharmacopoeial criteria over 28 days.

3.7 Factors affecting microbial preservative efficacy

Preservative efficacy is a property of the whole formulation, not of the preservative alone, and the factors are a standard examination list:

- **pH:** organic acids work only where they are undissociated (acid pH); parabens hydrolyse in strong alkali; every system has a pH window.
- **Partitioning into the oil phase:** preservative dissolved in oil droplets or solubilised inside surfactant micelles is absent from the water phase where microbes live; high oil loads and high surfactant levels can quietly strip a system.
- **Inactivation by ingredients:** nonionic surfactants and some polymers bind or solubilise preservatives; cationic preservatives are neutralised by anionic ingredients.
- **Concentration and water activity:** the free aqueous concentration does the work; high solids and humectant loads lower water activity and help.
- **Container and closure:** permeable or wide mouthed packs admit contamination and may absorb preservative into plastic or liner materials.
- **Temperature and storage:** hydrolysis and volatilisation deplete preservative over shelf life, so efficacy must survive to the expiry date, not just pass at release.

- **Initial bioburden and manufacturing hygiene:** a preservative system is designed to control incidental contamination, not to rescue a dirty batch.

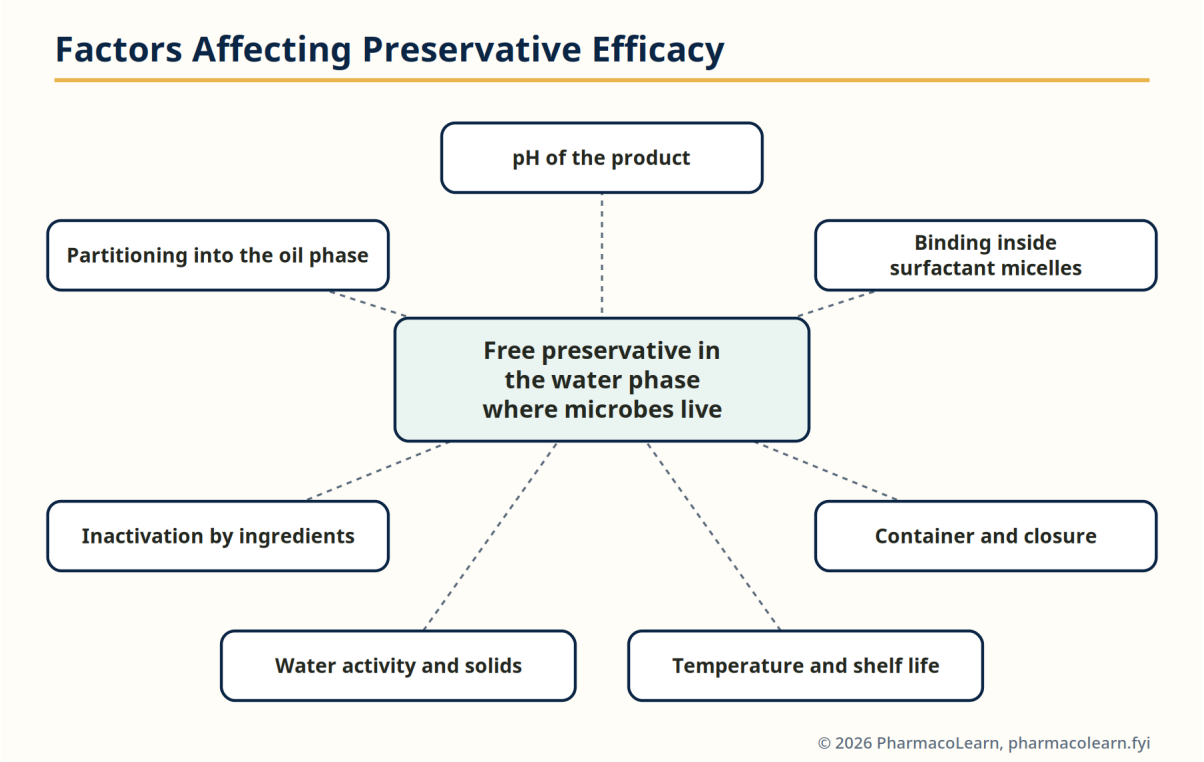

Figure: Preservative efficacy is decided by the whole formulation. Every factor shown moves preservative out of the water phase where microbes live.

3.8 Building blocks of a moisturizing cream

A moisturizing cream is an oil in water emulsion organised around the three dry skin mechanisms of Unit 2. Its blocks: an aqueous phase of water with **humectants** (glycerin is the standard, supported by propylene glycol, sorbitol, urea at cosmetic levels and hyaluronic acid in premium products) that bind water in the stratum corneum; an **oil phase** of emollients, including an occlusive component such as petrolatum or mineral oil that cuts TEWL; an **emulsifier system**, commonly a nonionic pair or a fatty alcohol and soap combination, holding the emulsion; **rheology** from cetyl and stearyl alcohols and a polymer for body; **preservative system, chelator, antioxidant, fragrance** and pH adjustment to about skin pH. Barrier repair variants add the stratum corneum's own lipids, ceramides, cholesterol and fatty acids, in the ratios the skin uses. The formula logic is additive to the biology: occlude, hydrate, smooth, and do not damage the barrier with harsh surfactants or excess fragrance.

3.9 Building blocks of a vanishing cream and a cold cream

These two classical creams are the cleanest illustration in the subject that emulsion type and emollient choice are the product.

Feature	Vanishing cream	Cold cream
Emulsion type	Oil in water	Water in oil (classically)
Core building blocks	Stearic acid partly neutralised in situ with potassium hydroxide or triethanolamine to form a soap emulsifier, with glycerin as humectant and water as the bulk phase	Beeswax and borax, whose reaction forms a soap emulsifier in situ, with a large mineral oil phase and water dispersed within it

Feature	Vanishing cream	Cold cream
Behaviour on skin	Rubs in and seems to vanish, leaving a dry, matte, slightly powdery stearic acid film; a base for powders and make up	Feels cool as the dispersed water evaporates, leaves a rich occlusive film; a cleanser and night cream base
Feel and use	Light, non greasy, daytime	Heavy, greasy, for dry skin, massage and make up removal

Both are made by the same in situ soap trick with opposite geometry: in the vanishing cream a small amount of oil phase (stearic acid) is emulsified into much water; in the cold cream a small amount of water is emulsified into much oil. Modern versions replace the soap systems with nonionic emulsifiers for stability and pH control, but the block diagrams examiners ask for are the classical ones above.

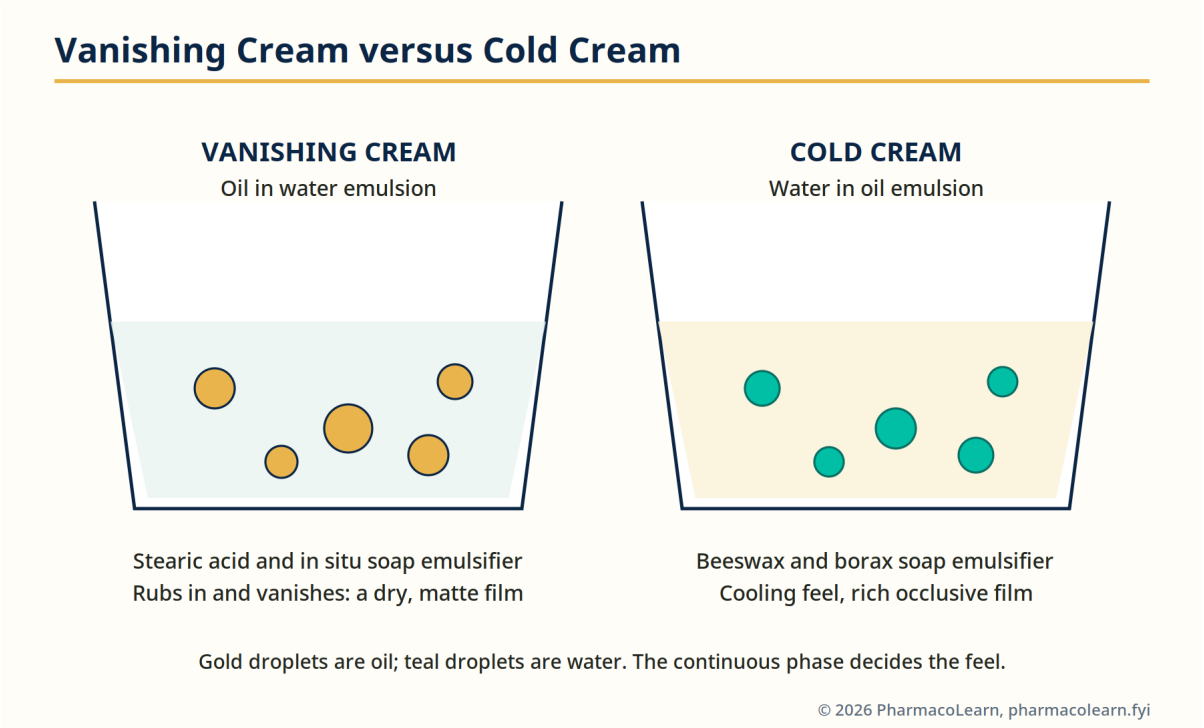

Figure: The same in situ soap trick in opposite geometry. Which phase is continuous decides whether the cream vanishes or coats.

3.10 Building blocks of a shampoo

A shampoo is a surfactant system built to clean hair and scalp without stripping either into damage. Blocks: a **primary anionic surfactant** for detergency and foam (sodium laureth sulfate is the industry standard; sodium lauryl sulfate the stronger, harsher alternative); a **secondary amphoteric surfactant** (cocamidopropyl betaine) to moderate irritation and stabilise foam; **foam boosters and viscosity control** (sodium chloride response of the micellar system, or polymeric thickeners); **conditioning agents** matched to the variant: cationic guar or polyquaternium polymers and silicones such as dimethicone in conditioning shampoos, deposited from the wash liquor onto damaged hair; an **opacifier or pearlescer** (glycol distearate) where a creamy appearance is wanted; **preservative, chelator, fragrance, colour and pH adjustment** to a mildly acidic pH that keeps the cuticle flat. Specialised variants are built by swapping one block: anti dandruff shampoos add the antifungal actives of Unit 4; baby shampoos rebuild the surfactant system around amphoterics and nonionics for mildness. The formulation tension is constant: cleaning power lives in the same surfactant aggressiveness that irritates scalp and strips hair, so shampoo design is the management of a compromise.

3.11 Building blocks of a toothpaste

A toothpaste is a structured aqueous gel carrying a high load of solid abrasive. Blocks: **abrasives** (hydrated silica is the modern standard; calcium carbonate and dicalcium phosphate the classical alternatives) at levels giving cleaning without excessive enamel and dentin wear; **humectants** (sorbitol solution, glycerin) keeping the paste from drying in the tube and giving body; **water**; a **binder or rheology system** (carboxymethylcellulose, xanthan or carrageenan, often with colloidal silica) suspending the abrasive and giving the ribbon its stand up; **surfactant** (sodium lauryl sulfate) for foam and dispersion; **fluoride** where the product is positioned for caries protection (sodium fluoride or sodium monofluorophosphate, the anticaries active, whose status as drug or cosmetic varies by market and claim); **flavour** (peppermint and menthol systems strong enough to mask raw materials and signal freshness); **sweetener** (saccharin), **preservative**, opacifier (titanium dioxide) and colour. The design constraints are pharmaceutical in character: abrasive and fluoride must stay uniformly dispersed for the tube's life, fluoride must remain bioavailable and not be bound by an incompatible abrasive, and the rheology must extrude as a clean ribbon yet break down instantly in brushing.

3.12 Soaps and syndet bars

A soap is the sodium or potassium salt of fatty acids, made by saponifying fats and oils with alkali; the fatty acid profile of the feedstock writes the bar's properties, hard saturated fats such as tallow and coconut giving hardness and lather, unsaturated oils giving mildness at the cost of softness and rancidity risk. Soap cleans by its surfactant action but carries two built in weaknesses: its solutions are alkaline, around pH 9 to 10, against the skin's acid mantle, and it forms insoluble lime soap scum in hard water. A **syndet bar** (synthetic detergent bar) replaces all or most of the soap with synthetic surfactants such as sodium cocoyl isethionate, allowing a skin neutral pH around 5.5, good performance in hard water, and a milder profile suited to facial and sensitive skin cleansing. Combination bars blend soap and syndet for cost and feel. The comparison is a guaranteed examination item:

Feature	Soap bar	Syndet bar
Cleansing agent	Fatty acid salts from saponification	Synthetic surfactants, e.g. sodium cocoyl isethionate
pH in use	Alkaline, about 9 to 10	Near skin pH, about 5.5 to 7
Hard water behaviour	Forms scum, loses lather	Lathers normally
Mildness	Can strip lipids and raise skin pH for hours	Milder, preferred for face and sensitive skin
Cost and tradition	Cheapest, oldest cleanser	Dearer, modern positioning

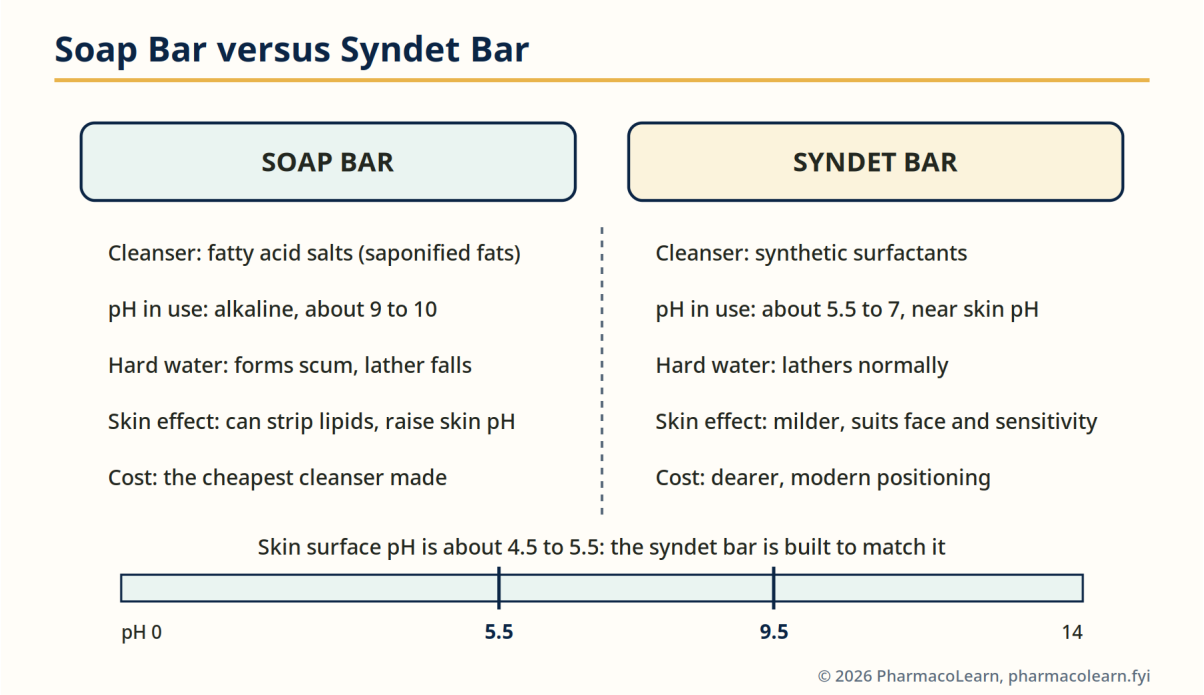

Figure: Soap and syndet bars compared. The pH strip shows the syndet bar's design target: the skin surface itself.

3.13 Perfumes: classification and the EU allergen rules

Perfume is a composition of fragrant materials in an alcoholic or oil base, and cosmetics borrow both its materials and its vocabulary. Classified by concentration of the fragrance compound, the traditional grades run: **parfum (extrait)**, the strongest at roughly 15 to 30 percent compound; **eau de parfum**, about 10 to 20 percent; **eau de toilette**, about 5 to 15 percent; and **eau de cologne**, about 2 to 5 percent, percentages varying by house and source. Classified by odour family, perfumes group into floral, oriental (amber), woody, fougere, chypre and citrus or fresh families, and by structure every fine fragrance is described as top notes (volatile, first impression), heart or middle notes (the character), and base notes (the fixatives that persist). Within cosmetics, fragrance is dosed far lower, in the tenths of a percent in a cream to a few percent in a soap, and serves product identity and the masking of base odours as much as perfuming the user. Regulation meets perfume at allergens: the EU Cosmetics Regulation requires that 26 named fragrance allergens be declared individually on the label when present above 0.001 percent in leave on products or 0.01 percent in rinse off products. The classic members of that list include limonene, linalool, geraniol, citronellol, citral, eugenol, coumarin, benzyl alcohol, cinnamal and hydroxycitronellal. The labelling logic is the point the syllabus tests: these materials are not banned; they must be declared so that sensitised consumers can avoid them, and a formulator using natural essential oils inherits their allergens automatically, because the oils contain them.

3.14 Controversial ingredients: parabens, formaldehyde liberators and dioxane

Three ingredient groups carry a public controversy that a formulator must discuss with evidence rather than slogans, and the syllabus names them exactly.

Parabens. The paraben preservatives (section 3.6) were challenged after studies showed weak estrogenic activity in vitro and a widely reported 2004 paper found parabens in breast tumour tissue without establishing any causal link or comparison tissue. Regulatory reviews by the EU's scientific committees concluded that methyl and ethyl paraben remain safe at permitted levels, while propyl and butyl paraben were restricted to lower levels and a few longer chain parabens were removed for lack of data. The balanced position: parabens are among the best characterised and least sensitising preservatives known, and the controversy is a risk perception problem more than a demonstrated harm problem at cosmetic

doses. "Paraben free" reformulation has often replaced them with less characterised or more sensitising alternatives, the isothiazolinone sensitization epidemic being the standing warning.

Formaldehyde liberators. Preservatives such as DMDM hydantoin and imidazolidinyl urea work by slowly releasing formaldehyde. Formaldehyde is an established contact allergen and, in industrial inhalation exposure, a carcinogen; the liberators therefore sit under permanent pressure. Their defence is dose and route: the free formaldehyde in a preserved rinse off product is very low, and patch test data put sensitization rates at low single digit percentages of dermatitis patients. The EU requires a "contains formaldehyde" warning above a threshold of free formaldehyde in the finished product. The honest summary is that the hazard is real, the exposure is small, and sensitive individuals are protected by labelling.

Dioxane. 1,4-Dioxane is not an ingredient at all: it is a trace byproduct formed during the ethoxylation that makes mild surfactants such as sodium laureth sulfate, and it appears on controversy lists because it is a possible carcinogen in animal studies at high doses. Control is by manufacturing: vacuum stripping of ethoxylated raw materials reduces residual dioxane to low parts per million, and regulators monitor it as an impurity limit rather than an ingredient decision. The three cases together teach the unit's lesson: distinguish hazard from risk, ingredient from impurity, and evidence from alarm, because the next controversial ingredient will arrive by the same route.

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