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CLAYS IN COSMETICS AND PERSONAL-CARE PRODUCTS

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Abstract—Clays are used in various cosmetic formulations, such as sunscreens, toothpastes, deodorants, creams, hair cosmetics, makeups, nail polish, facial masks, and shampoos, among others, to improve the organoleptic and physicochemical characteristics, to increase the stability, or to facilitate elaboration. Together with their technological functionalities, clays are cosmetologically active ingredients with cleaning, anti-aging, anti-wrinkling, and sun-care functionalities. Talc, kaolinite, mica, and some smectites are the clay minerals used most frequently in cosmetic products, but several other phyllosilicates as well as modified and synthetic clays are also used. Sometimes, clays are useful in the design of cosmetics just because they are made of rigid, small, and anisometric particles. Kaolinite and mica are made of hard prismatic particles which are lightly abrasive over the skin, teeth, or hair. Electric charges in smectites result in ion-exchange capacities useful in the loading of active cosmetics but also adsorbing and cleaning waste substances. Intermediate net negative charges of smectites result in layer expansion in polar media and specific rheological properties that are very useful in cosmetic formulations. The absence of charged particles in talc and kaolin make them flow easily resulting in lubricant effects. Protection against radiation from the sun by clay particles and decorative effects complete the possibilities of clays in cosmetics. The nomenclature for clays used as ingredients in cosmetics follows historical use and the names of commercial products, rather than following strict compositional principles. In this sense, an effort was made here to correlate the names of the minerals that make up each of the clay-based cosmetic ingredients.

Keywords—Clays and clay minerals · Cosmetics · Cosmetological functions · INCI names · Phyllosilicates · Trade names

INTRODUCTION

The design, development, control, and convenient use of health-care products, especially cosmetics, are amongst the objectives of 'pharmacy.' These products are not natural, but are mainly fabricated with natural materials, including minerals and, in particular, clays. Clays are used in the manufacture of cosmetics because they possess characteristics which help to generate the desired and useful technological properties, and also because they can participate in the effects of the products when they are applied (cosmetological properties). Clay characteristics are used to improve technical properties, e.g. increase the stability of emulsions and the viscosity of suspensions (Viseras et al., 2007). Clays also provide specific functions to the cosmetics, including solar protection, water-loss reduction, and cleaning of skin and hair (Viseras et al., 2019). Clays are, therefore, both technological additives and cosmetologically active ingredients in cosmetic products (López-Galindo et al., 2007; Viseras et al., 2007, 2019; Carretero & Pozo, 2009, 2010). Clay functionalities in cosmetics result mainly from their surface properties (surface area, cation exchange capacity, layer charge, among others); rheological properties (thixotrophy, rheopexy, viscosity, plasticity), and other physical and mechanical properties including particle size, shape, color, softness, opacity, reflectance, iridescence, etc. (Moraes et al., 2017).

The global cosmetic ingredients market is valued at approximately €30 billion (US$35 billion)/year, and is led by western Europe and North America, accounting for half of the market share. The cosmetic products made from these ingredients retailed for a total of €80 billion (US$92 billion) in Europe (2019), thus making it the largest cosmetics market in the world (Cosmetic Europe, 2019).

Cosmetics include a heterogeneous group of products, including everyday hygiene products such as soap, shampoo, deodorant, and toothpaste but also beauty items such as perfumes and makeups. Distinguishing between cosmetics and other products for human health care is not easy. The difficulty lies mainly in the type of substances used to make cosmetics, which are very often the same as those used in the formulation of other health-care products of different categories. In particular, clays, given their ubiquity, low cost, and special properties derived from their structure, are used widely in formulations and products with different purposes. The attributes that determine the quality of a particular clay ingredient (identity, purity, and richness) will be different depending on

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the product's purpose, so that the same mineral may appear in different products, although the use requirements will be different.

COSMETIC INTENDED USE AND COSMETIC TYPES

A cosmetic is defined in Europe as "any substance or mixture intended to be placed in contact with the external parts of the human body (epidermis, hair system, nails, lips, and external genital organs) or with the teeth and the mucous membranes of the oral cavity with a view exclusively or mainly to cleaning them, perfuming them, changing their appearance, protecting them, keeping them in good condition, or correcting body odors (Regulation (EC) No 1223/2009, n.d.). In the USA, cosmetics are also defined in view of their purpose, as "articles intended to be rubbed, poured, sprinkled, or sprayed on, introduced into, or otherwise applied to the human body . . . for cleansing, beautifying, promoting attractiveness, or altering the appearance" (Federal Food, Drug, and Cosmetic Act, 2021). Consequently, cosmetics are clearly distinguished from medicinal products (Europe) or drugs (USA), as these are used in the diagnosis, cure, mitigation, treatment, or prevention of diseases. It is important to note that the difference between a cosmetic product and a medicinal product is the intention of use, so that two products identical in composition and form may be considered to be different. Some interesting examples are the use of essential oils for perfuming (cosmetics) or aromatherapy (medicinal product), as well as the use of a massage cream to hydrate the skin (cosmetic) or to relieve muscle pain (medicinal product). To complicate the situation further, there are two other products used for health care that have a place in the legislation and the objectives and/or mechanisms of action of which are different from those of cosmetics or medicinal products. These are medical devices and dietary supplements. Medical devices have the same indications as medicinal products (diagnosis, cure, mitigation, treatment, or prevention of disease) but differ in the mechanisms to achieve these, as medical devices do not work by any pharmacological, biochemical, or metabolic pathway (as medicinal products do). Dietary supplements (USA) or food supplements (Europe) are those products taken by mouth that contain a 'dietary ingredient' intended to supplement the diet. Each of these four products (medicinal product, medical device, dietary supplement, and cosmetic) has different regulations with different approval, registration, manufacturing, and labeling requirements. Detailed information can be found on the websites of the two public bodies dealing with these products in Europe (European Medicines Agency, 2021) and the United States (Food and Drug Administration, 2021). On occasion, it is difficult to discern the corresponding category of a certain product, especially when it accomplishes mechanisms, intended uses, or ingredients of other categories at the same time. A fifth group of products exists which covers 'borderline' products and which includes those healthcare products for which uncertainty exists about the regulatory framework that applies (Manual on borderline and classification in the community regulatory framework for medical devices, 2019). The intended uses of cosmetics are limited to cleaning, perfuming, and changing appearance, protecting, keeping in good condition, or correcting body odors. If the promotional information of a cosmetic drives the consumer to use it for a purpose other than those indicated, the product is no longer a cosmetic. Consequently, any claim or statement that may induce the consumer to expect (for instance) a reduction in cellulite or a regeneration of skin cells are forbidden in cosmetics. It is also forbidden to include ingredients that may cause the product to be considered a therapeutic substance (e.g. fluoride in toothpastes). The poorly defined limits between products result in frequent warning letters advising of an incorrect use of a product (Federal Food, Drug, and Cosmetic Act, 2020; Food and Drug Administration, 2020).

The European cosmetic directive 76/768/ECC lists, in Annex I, the recognized cosmetic products in the European market (Council Directive 76/768/EEC, 2009). This heterogeneous list can be divided (Table 1) according to three major classification criteria: the place of application, the purpose, and the shape or consistency. The European association of cosmetic fabricants classifies cosmetics in seven categories (Cosmetic Europe, 2019): those applied to the hair to clean it, protect it, and keep it in good condition (hair-care products); those applied to teeth and the oral cavity (oral-care products), skin (skin-care products), or the body in general (body-care products). Moreover, some cosmetics have a much more specific purpose, as happens with deodorants (to correct body odors), sunscreens (to protect the body from sun), decorative cosmetics (intended to change the appearance of different body parts), or perfumes (to alter the body odors). These specific cosmetics can be used independently (on their own) or be part of other cosmetics, as typically happens with perfumes.

CLAYS AS INGREDIENTS IN COSMETICS

Clays have been used for cosmetic purposes since prehistoric times (Carretero, 2002). There is evidence of the use of clays to modify appearance in prehistoric rituals, including body painting. Many indigenous populations continue to use clays for their rituals (Mpako et al., 2011), being fundamental ingredients in what could be called ethnocosmetics; e.g. the elaborate hairstyle of the Hamer community from Ethiopia made with clay and butter (Fig. 1) or the Suri earlobe discs, facial painting, and hairstyle (Abbink, 2009).

Without detracting from the importance of these uses, the current study is focused on the use of clays and derivatives as ingredients in commercial cosmetics products. A wide range of cosmetics products containing clay minerals in their composition has been designed throughout time and most of them have been patented. The use of a substance as a cosmetic ingredient requires, first, its precise identification. The Regulation (EC) No 1223/2009, in Article 33, states that the Commission shall compile and update a glossary of common ingredient names (CINs) employed in cosmetic products (CosIng, 2021).

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Table 1. Types of cosmetics

Cosmetics categories *	Cosmetics products **
Skin/body care products	Creams, emulsions, lotions, gels, and oils for the skin (hands, face, feet, etc.).
	Face masks (with the exception of chemical peeling products).
	Anti-wrinkle products.
	Products for external intimate hygiene.
Hair care products	Tinted bases (liquids, pastes, powders).
	Hair-care products including hair tints and bleaches, products for waving, straightening and fixing, setting products, cleansing products (lotions, powders, shampoos), conditioning products (lotions, creams, oils), and hairdressing products (lotions, lacquers, brilliantines).
Oral-care products	Products for care of the teeth and the mouth.
Sun-care products	Sunbathing products.
	Products for tanning without sun.
Deodorants/perfumes	Toilet soaps, deodorant soaps, etc.
	Bath and shower preparations (salts, foams, oils, gels, etc.).
	Perfumes, toilet waters and eau de Cologne.
	Deodorants and anti-perspirants.
Decorative cosmetics	Make-up powders, after-bath powders, hygienic powders, etc.
	Products for nail care and make-up.
	Products for making-up and removing make-up from the face and the eyes.
	Products intended for application to the lips.
	Depilatories.
	Shaving products (creams, foams, lotions, etc.).
	Skin-whitening products.

*Categories according to the European association of cosmetics fabricants (https://cosmeticseurope.eu/cosmetic-products/).

**Types according to European cosmetics directive 76/768/ECC list in annex I.

Together, the INCI (International Nomenclature Cosmetic Ingredient) names, developed by the International Nomenclature Committee and published by the Personal Care Products Council in the International Cosmetic Ingredient Dictionary and Handbook (Nikitakis & Lange, 2016; PCPC, 2021) are used to identify uniformly the substances in cosmetic labels. Note that the assignment of an INCI name to an ingredient does not imply that the ingredient complies with a particular national or international regulation. Manufacturers and/or suppliers usually assign Trade Names (TN) to their cosmetic ingredients that can be different for the same ingredient supplied by different companies. Manufacturers and suppliers can assign a 'Trade Name Mixture' to identify a particular blend of cosmetic ingredients that cannot be used for labeling purposes; the INCI name of each individual component of the mixture must be listed separately.

Phyllosilicates with different layer types, net negative charges, or chemical compositions are used widely in cosmetic formulations (Fig. 2). Talc, kaolin, mica, and bentonite stand out for being the most used, but many other clays are used frequently, providing the formulations with advanced functions. To classify the clays and clay minerals used as cosmetics ingredients, the classification proposed by Martin et al. (1991) has been taken as the starting point and updated by the nomenclature committee of AIPEA (Association Internationale pour l'étude des Argiles - international clay organization) in 2006 (Guggenheim et al., 2006). Two extra sections with synthetic clays and those clays with a trade name that do not correspond to a specific mineral have also been included.

Zero-Charge Phyllosilicates

Both talc and kaolinite are often included in hair-care formulations such as shampoos and hair masks intended to treat 'oily hair.' The oil-absorbing capacity of clays is a result of their large specific surface area and makes them particularly interesting ingredients in these formulations. Three INCI ingredients contain kaolinite (Table 2). Note that both Fuller's earth and Solum fullonum have been included here according to their cosmetic ingredient description. Nevertheless, these names are well known to correspond to other minerals (smectites and/orpalygorskite-rich rocks) in the mining industry. Kaolin is used in 1700 cosmetic patents whereas 34 patents of cosmetics (most of them in the last century) cite Fuller's earth as the ingredient, described as a mix of kaolinite and smectites. High viscosity and thixotropic properties are desirable in several cosmetics formulations. For example, shampoo

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Fig. 1. Hairstyle of the Hamer community, Ethiopia

is expected to present high consistency at rest, avoiding separation of the constituents, but a significant decrease in viscosity when stress is applied to ease product application. In concentrated clay suspensions, the aggregation of particles by different mechanisms (depending on the type of clay minerals, pH, and ionic strength) is known to result in thixotropic and high-viscosity gels. The number of patents using these minerals has increased significantly in the last century, the main applicant companies being Oreal® and Procter and Gamble®.

In the 21st century, kaolin has been used in makeup formulations (Kim & Kim, 2012; Choi et al., 2013), powder masks (Kim, 2007, 2009), as well as in makeup-removal products (Braunagel et al., 1997; Koely-Therouin & Mattei, 2001). Synthetic kaolin was proposed by the Sekisui Company to formulate color masks (Nishi, 2001). The effectiveness of kaolinite and montmorillonite as vehicles for the administration of certain active ingredients was shown by Hamilton et al. (2019) to improve acne affections. Peel-off mask gel formulations have been developed with Aloe Vera and kaolinite (Beringhs et al., 2013) or montmorillonite (Asthana et al., 2021). The ability of emulsions formulated with *Litchi chinensis* leaf ethanolic extract in combination with kaolin to prevent UVB-induced photodamage was studied by Thiesen et al. (2020).

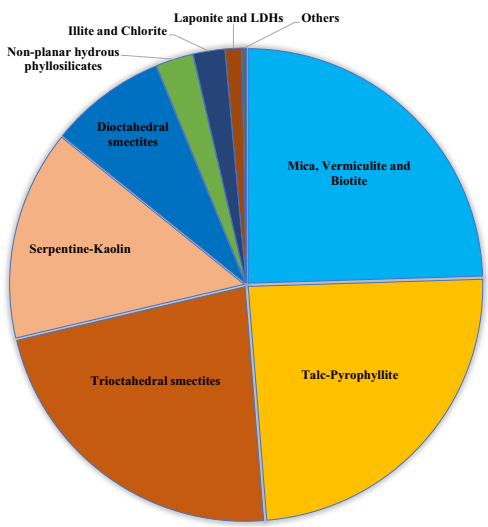

Fig. 2. Distribution of patent applications for cosmetics which include clays

For 2:1 layer phyllosilicates with zero net negative charge, talc is the cosmetic ingredient used most often, with >3000 patents. Talc is used as an emulgent in 'makeup preparations' because of its large surface area. Unlike other clay minerals, the structure and properties of talc make it particularly useful to improve the flow and softness of solid powdery mixtures, rather than in the form of aqueous dispersion. Talc has been proposed recently as a color booster and to enhance the cohesion and coverage of skin powders (Dumousseaux, 2011; Meli & Pagis, 2018). Similarly, pyrophyllite has been also proposed with similar features (Chae & Kim, 2012; Kim et al., 2012). Likewise, talc has been formulated with butane to obtain aerosol-moisturizing formulations (Kang et al., 2004). Opacity effects and skin protection are also important functions of talc in cosmetic formulations (Kaida et al., 2004), as well as its abrasive and adsorptive functions in shaving formulations (Albrecht & Stelzer, 2003; Kohut & Ruppert, 2004). Nanoparticulate synthetic talc combined with nanoparticulate silica was used as a filler for polymers (Wittmer, 2002) or to adsorb ultraviolet protection actives in sun-protecting formulations (Arseguel et al., 2000). Synergistic effects can be obtained by modifying or combining talc with other minerals such as mica (Hechavarria, 1994; Iida & Nishimura, 1998).

Smectites

Both dioctahedral and trioctahedral smectites are used as cosmetic ingredients (Table 3). Raw hectorite and organically modified hectorite are used as rheology modifiers, gel-forming agents, and bulking additives in several cosmetic formulations. Together, stevensite (INCI name = 'Moroccan lava clay') as well as saponite are useful as cleansing and conditioning hair-product ingredients. About 600 cosmetic patents use hectorites, of which 61 are quaternium-18 hectorite, 71 are stearalkonium hectorite, and 79 are disteardimonium hectorite. Hectorite has been included in the lipid phase of a semisolid cleansing emulsion (Koopmann et al., 2006). Stearalkonium hectorite (0.01 to 0.1% by weight) has been included in lipid-based compositions such as lipsticks (Mendoza, 2015), whereas quaternium-18 hectorite is used as a non-surfactant dispersing agent at 2.5% w/w. A deodorizing cosmetic agent in the form of a suspension, containing 1.0–35 wt.% quaternium-18 hectorite was patented by Doring (2017).

Stevensite is used as a cosmetic ingredient, under its INCI name, in 56 cosmetic patents. Due to their superb cleaning properties, both stevensite and saponite have been used for centuries as a natural soap and shampoo. In fact, they are included in currently commercialized skin/body and hair-care

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Table 2. Zero net charge phyllosilicates used as cosmetic ingredients

Mineral Group	Minerals	INCI name	Description	Functions
Serpentine-kaolin	Kaolinite	Kaolin	Naturally occurring substances, kaolin	Abrasive, absorbent, anticaking, bulking, colorant, opacifying
	Kaolinite + smectite	Fuller's earth	A non-plastic variety of kaolin containing an aluminum magnesium silicate.	Abrasive, absorbent, bulking, opacifying
	Kaolinite + smectite	Solum fullonum	Fuller's Earth is a non-plastic variety of kaolin containing an aluminum magnesium silicate	Absorbent, anticaking, bulking, gel forming, opacifying, viscosity controlling
Talc-pyrophyllite	Pyrophyllite	Pyrophyllite	-	Abrasive, absorbent, opacifying
	Talc	Talc	-	Abrasive, absorbent, anticaking, bulking, opacifying, skin protecting
	Modified talc	Magnesium/potassium/silicon/ fluoride/hydroxide/oxide	Product obtained by heating talc with potassium silicofluoride	Bulking
		Ceria/silica talc	Carbonic acid, cerium (3+) salt, calcination products with silica and talc ($Mg_3Al_2(SiO_3)_4$)	UV absorber

products, e.g. Himalayan charcoal purifying glow mask© (The Body Shop®) or Moroccan black soap© (Savon Stories®).

Dioctahedral smectites (mainly montmorillonite, but also beidellite and nontronite, for example) are important ingredients in skin-care cosmetic products. They are used widely in facial-mask formulations as their large absorption/adsorption capacities allow them to remove sebum, dirt, toxins, and dead cells. Facial masks are made with clays because of their cleansing, astringent, exfoliating, and lifting effects. Skin masks usually have pseudoplastic properties for easy application, a rheological behavior that can be achieved by incorporating smectites. Bentonite is used in 1151 cosmetics patents, 46 of which are related to quaternium-18 bentonite, 10 to quaternium-90 bentonite, and 30 to stearalkonium bentonite. Together, montmorillonite is specified in 597 patents, whereas the number of patents with beidellite or nontronite are 69 and 49, respectively.

Bentonite was used as an emulsifier in a nail-enamel remover (Carter, 1940), in oil-in-watermake-up (O/W) (Gabriel, 1973), vanishing low oil-content creams (Alexander, 1973),

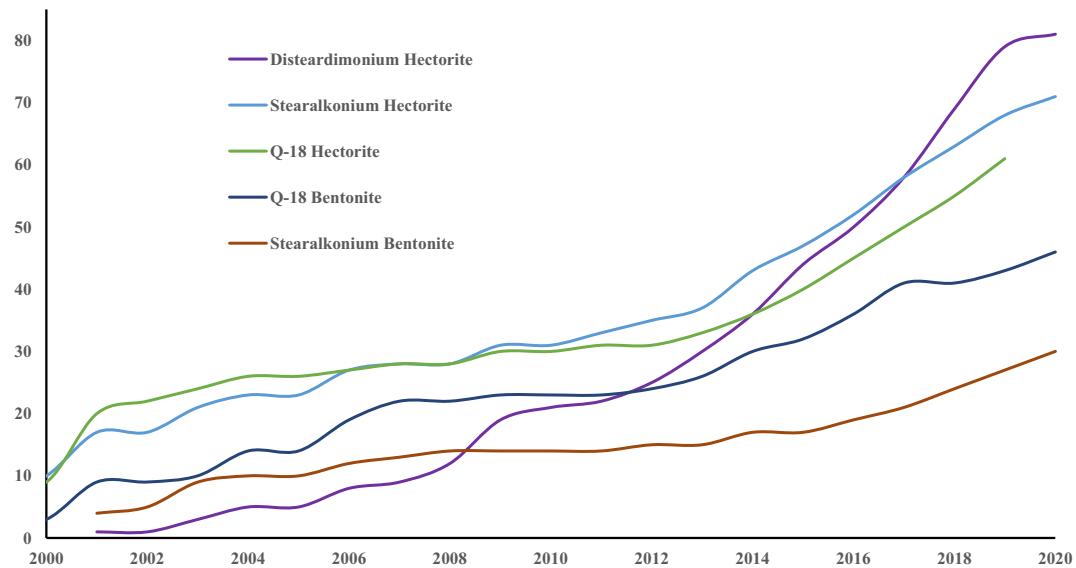

Fig. 3. Trends in terms of the top five organoclays included in the patent applications for cosmetics (over the period 2000–2020)

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Table 4. Minerals from the vermiculite, mica, and interlayer-deficient mica and chlorite groups used as cosmetic ingredients

Minerals	INCI name	Description	Functions
Vermiculite	Vermiculite	A phyllosilicate mineral consisting chiefly of oxides of silicon, aluminum, magnesium, calcium and iron.	Skin conditioning
Mica	Mica	Series of silicate minerals of varying chemical composition but with similar physical properties. Mica may have well-defined cleavage and split into very thin sheets.	Anticaking, bulking, colorant, opacifying
Non-specified mineral from mica group	Biotite	Micaite, rock-forming material of the mica-group	Bulking, viscosity controlling
Illite	Illite	Clay mineral having an intermediate composition between montmorillonite and muscovite	Abrasive, absorbent, anticaking, bulking
	Illite extract	The extract of illite	Skin conditioning
Chlorite	-	-	absorbent, anticaking, bulking

and in cleansing lotions (Sarfaraz, 2016). Bentonite particles accumulate around the internal drop's phase of emulsions and decrease the interfacial tension between the two insoluble liquid phases, avoiding their coalescence, phase separation, and emulsion breakage. The mechanisms of emulsification with clay particles and the formation of Pickering emulsions were studied deeply by Abend and Lagaly (2001) and most recently reviewed by Machado et al. (2019). Bentonite has been used in makeup products (Kim et al., 2003) and montmorillonite as a stabilizing agent in cosmetic emulsions (Calello et al., 2006) and as a sebum remover (Ko et al., 2010). The optimization of a peel-off, facial-mask formulation containing smectite and aloe vera was studied by Beringhs et al. (2013). More recently, a dry shampoo composition comprising a smectite, natural starches, and a natural-oil absorbent was developed and subsequently patented (Perfitt & Carimbocas, 2017). Face masks with bentonite, starch and polyvinyl alcohol were formulated by Chakraborty et al. (2019). Some formulations also included zinc oxide, which acts as a UV filter, or silver nanoparticles and gold nanoparticles, with antibacterial properties. Bentonite has been modified to quaternium-18 bentonite to stabilize oil in water (O/W) emulsions by Yang (2015) and combined with polymers to retain a chemical oxidizing agent in a hair-lightening product (Delostal & Seneca, 2019). Quaternium-18 bentonite is used in eyebrow pencil, eyeliner, eyeshadow, eye lotion, and other eye-makeup preparations, as well as in lipstick and aerosolized deodorant formulations (up to 0.6%). More recently, bentonite has been proposed as an anti-aging cosmetic ingredient due to an induction of telomerase activity (Bae et al., 2021). Both trioctahedral and dioctahedral smectites, with high refractive indices and optimal light dispersion properties, have been included in sunscreens, acting as a physical barrier that blocks the solar radiation and protects the cellular nucleic acids (Ghadiri et al., 2014; Mattioli et al., 2015). Smectites are also used as natural eye shadow, blush powder (Gamoudi & Srara, 2018), and facial makeup (Cavalcanti et al., 2018).

The main companies using natural smectites are Oreal® and Shiseido®, whereas Amorepacific®, Henkel AG®, LG Household®, and Beiersdorf AG® are the applicants using organically modified smectites.

Decorative nail polishes consist of a polymeric base, usually made of nitrocellulose, solvents, plasticizers, and pigments. Modern gel nail polishes contain a suspension

Table 5. Non-planar hydrous clay minerals used as cosmetic ingredients

Minerals	INCI name	Description	Functions
Sepiolite	Sepiolite	Meerschaum	Viscosity controlling
	Sepiolite extract	Extract of sepiolite	Skin conditioning
	Benzalkonium sepiolite	The product obtained by the reaction of benzalkonium chloride and sepiolite	Emulsion stabilizing, viscosity controlling
	Quaternium-90 sepiolite	The product obtained by the reaction of quaternium-90 and Sepiolite	Emulsion stabilizing, viscosity controlling
	Magnesium trisilicate	-	Abrasive, absorbent, anticaking, bulking, opacifying, viscosity controlling
Palygorskite	Attapulgite	Palygorskite	Abrasive, absorbent, bulking, opacifying, viscosity controlling
Halloysite	Halloysite	$Al_2Si_2O_5(OH)_4$	Absorbent, anti-sebum, colorant, viscosity controlling

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system, frequently based on modified organic clays able to solve stability issues, specifically pigment sedimentation and syneresis (Grigale-Soročina et al., 2017; Kovalenko et al., 2017; Grigale-Soročina & Birks, 2019). Alkali and alkaline earth metals in smectites may be exchanged easily with quaternary ammonium chloride cations, covalently bonded to aliphatic chains, aromatic rings, and/or other functional groups, to obtain organophilic clays. This cation exchange shifts the nature of these minerals from hydrophilic to lipophilic. Different organoclays can be obtained by changing the negative charge density of the clay mineral and, therefore, the packing density of the alkyl chains (Lagaly & Dékany, 2005). Organomodified clays such as smectites (montmorillonite, hectorite) and organomodified sepiolite (organoclays) have been used widely as cosmetic ingredients, acting as dispersing agents, emulsion stabilizers, and viscosity enhancers (Fig. 3).

Table 6. Other clays and related materials used as cosmetic ingredients

Mineral	INCI name	Description	Functions
Laponite		Synthetic anionic clay	Emulsion stabilizing, viscosity-controlling, thickening agents, gelling agents and fillers
LDHs		Layered double hydroxides	Absorbent, protecting agent
	Sodium magnesium silicate	A synthetic silicate clay with a composition mainly of magnesium and sodium silicate	Binding, viscosity-controlling
Not specified mineral composition	Clay	A group of phyllosilicate minerals produced by chemical and physical weathering of rock. It consists chiefly of varying amounts of hydrated silica and alumina, and is characterized by a particle size of <2 μm	Absorbent, binding, bulking, skin-conditioning, viscosity-controlling
	Clay extract	The extract of clay	Skin-conditioning
	Clay mineral oxides	The product obtained by the calcination of clay minerals	Skin-conditioning
	Clay minerals	Are various minerals isolated from clay	Astringent, binding, buffering, humectant
	Activated clay	Inorganic compound obtained by heating natural aluminum silicate with sulfuric acid	Absorbent, bulking
	Aluminum silicate	Aluminatesilicate; Aluminosilicate	Abrasive, absorbent, anticaking, bulking, colorant, opacifying
	Calcium silicate		Absorbent, bulking, opacifying, pearlescent, viscosity-controlling
	Alluvial mud	Sediment deposit that contains silt and clay particles and is obtained near a river or other body of freshwater	Abrasive, binding
	Sea-clay extract	An extract of clay from the sea	Hair-conditioning, skin-conditioning
	Moonstone powder	Powder obtained from crushed moonstone, a gem classified as orthoclase feldspar and consisting of varying amounts of calcium, potassium and sodium aluminium silicates	Skin-conditioning
	Mudstone powder	The powder obtained from dried, ground mudstone. It is classified as sedimentary rock composed primarily of clay and silt sized materials depending on the degree of compression on the rock	Abrasive, buffering
	Volcanic soil	A mixture of minerals derived from volcanic deposits which are of varying size including but not limited to sand, silt and clay	Skin-conditioning
	Volcanic ash	An amorphous, inorganic silicate obtained from lava deposits	Abrasive, absorbent, bulking,
	CI 77004	An inorganic color. It consists of a natural hydrated aluminum silicate	Colorant

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Other 2:1 Planar Hydrous Phyllosilicates

High net layer charge (>0.6) planar phyllosilicates are also used as cosmetic ingredients (Table 4). Of this group of minerals, mica is the cosmetic ingredient used most often, being present in >2800 patents. Mica is used in makeup products (illuminators, powder makeup, lipsticks, or eye shadows) based on its ability to absorb and reflect light (Wuesteneck & Wuesteneck, 1984; Ikeda et al., 1986; Ando & Kosugi, 1989; Bajan et al., 2002; Kumagai et al., 2004; Choi et al., 2012; Cho et al., 2016). Mica has also been formulated with cyclodextrin (Coutelle et al., 1998), silicones (Koenig et al., 2006; Ricard & Kongmany, 2020), and camellia oil (Choi, 2017). Synthetic mica was proposed as a cosmetic ingredient (Ishikawa & Kuratani, 2000; Saeki, 2000) and used in sun products (Debacker, 2005) and eye shadows (Ando et al., 2006). Synthetic micas combined with L-arginine have been used to prepare moisturizing powders (Han et al., 2008) and, once modified (Abiko et al., 2011) or loaded with Zn (Nagahama, 2012), have been included in cosmetics. Mica is also included in many cosmetic formulations with sunscreen activity, not only because it protects against solar radiation, but because it also provides a shimmering effect on the skin (Su et al., 2014). The UV-Visible absorption ranges of some clays have been characterized in numerous studies (Babin & Stramski, 2004; Hoang-Minh et al., 2010). Sunscreen formulations based on mica and a biosurfactant extract were designed and characterized by Rincón-Fontán et al. (2018).

Table 7. Some examples of commercial cosmetic products with clays

	Commercial name of the product	Clay ingredient (INCI names)	Company
Facial Masks	Mask Tensoderm©	Kaolin Magnesium aluminium silicate	Viñas Laboratories ®
	Pure Clay-Purity Mask© Pure Clay-Glow Mask© Pure Clay-Detox Mask©	Kaolin Montmorillonite Moroccan lava clay	L´Oreal Paris®
	Mask of Magnaminty©	Hectorite Kaolin Talc	Lush®
	Himalayan Charcoal© Purifying Mask©	Kaolin Moroccan Lava clay Magnesium aluminium silicate	The Body Shop®
	Rhassoul Detox Mask©	Rhassoul clay	Savon Stories®
	Esmerald Clay facial mask©	Kaolin Hectorite	Freshly cosmetics®
Hair cosmetics	ELVIVE Extraordinary Clay Shampoo©	Magnesium aluminium silicate Montmorillonite Kaolin	L´Oreal Paris®
	Clay and Sulphur Shampoo©	Kaolin	Armonia®
	Green clay shampoo©	Green clay (montmorillonite)	Cattier®
Sunscreens	Anthelios Mineral One©	Stearalkonium hectorite	La Roche-Posay®
Nail polish	8-free Rosé Thé©	Steralkonium bentonite	Avril®
	Hot Summer©	Steralkonium bentonite Mica	Benecos®
	Holy Elephant 11©	Stearalkonium hectorite	Neobio natural cosmetics®
Makeup Powder makeup			
	Natural Finishing Podwer©	Mica	Freshly cosmetics®
	Radiant Loose Powder Foundation©	Mica Kaolin	Nude By Nature®
Lipstick	Moisture Lipstick©	Hectorite Talc Mica	SANTE naturkosmetik®
Deodorants	Anti-odorant nuud©	Stearalkonium bentonite	NUUD BV®
	Mandarin Deodorant©	Talc	KRIIM Lab. ®
Baby powders	Protective poder baby©	Solum Follonum (green clay)	Argital®
	Johnsons baby talc powders©	Talc	Johnson & Johnson®
Toothpastes	Pure FreshnessPure ©	Hectorite	Freshly cosmetics®
	Dentifricio alla Menta©	Solum Follonum	Antos®
	Refreshing Spearmint Toothpaste ©	Kaolin	KRIIM Lab®

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Vermiculite is used mainly in skin-conditioning products (>200 patents), whereas biotite, illite, and chlorite are cited in 59, 116, and 157 patents, respectively. Vermiculite has been included in cosmetics packs (Kim & Kim, 2004) and used as a sorbent (Atamaniuk, 2006). Illite has been included in skin ointments (Kim & Son, 2006), body-cleaning products able to absorb sebum exudates (Kim et al., 2008; Park, 2020), and as decorative color products (Do, 2013; Hyun et al., 2013). Illite has also been used in sun-care products (Ang et al., 2014) and anti-wrinkle products (Park, 2015), also in combination with artichoke leaf (rich in anti-aging polyphenols) (Do, 2021).

Non-planar Hydrous Phyllosilicates

Sepiolite (or magnesium trisilicate) is the non-planar clay mineral used most frequently in cosmetics (>150 patents), followed by palygorskite (attapulgite) with 111 cosmetic formulations, and halloysite (64 patents). These minerals are used with different technological functions derived from their particular structures (Table 5). Sepiolite, palygorskite, and halloysite have been proposed as carriers of compounds that absorb UV radiation (Del Hoyo et al., 2001; Suh, 2015). In recent years, palygorskite (Tang et al., 2020) and organically modified palygorskite (Cao et al., 2020; Huang, 2020) have been used in makeup formulations and sun-care products (Cho et al., 2013). Hair-care cosmetic formulations with halloysite loaded with other cosmetic ingredients have been designed (Shchukin et al., 2005; Suh et al., 2011; Santos et al., 2019; Sadjadi, 2020). The effective loading of dyes onto halloysite reduces the direct contact of the dye with the scalp, thus minimizing toxicity and possible allergic reactions. Suh and Cho (2015) developed TiO_2 nanoparticles on halloysite, obtaining suitable nanoparticle-halloysite hybrid powders for the formulation of sunscreens. Ascorbic acid loaded into halloysite nanotubes has also been proposed as a cosmetic product (Baschieri et al., 2019). A photoprotective treatment for hair, based on halloysite and keratin hybrid nanotubes, was developed by Cavallaro et al. (2020).

L'Oréal® is the main user of sepiolite and halloysite as cosmetic ingredients, whereas Procter and Gamble® is the major user of palygorskite in cosmetic products.

Other Clays and Related Materials

Synthetic materials with clay-like structures (such as Laponite®) or with structure in sheets similar to hydrotalcite (layer double hydroxides; LDHs) have also been used in cosmetics, mainly due to their ability to exchange cations or anions, respectively. Avon® has two patented formulations with Laponite® allowing the delivery of incompatible ingredients in a single formulation (Deleo et al., 2015; Howel et al., 2015). Layered double hydroxides, due to their ability to absorb, spread, and reflect UV radiation, are suitable structures to protect the photo or chemical activity of molecules, avoiding photo-instability and preventing direct contact with the skin (Franco et al., 2020). They have been used to design various color palettes of pigments, especially for nail-polish applications (Kovalenko & Kotok, 2020) (Table 6).

Other INCI denominations of clays or related materials that cannot be correlated to any specific minerals are listed in Table 6.

The treatment of a clay with sulfuric acid at elevated temperature results in an activated clay. This acid treatment creates discontinuities in both tetrahedral and octahedral sheets due to the partial dissolution of the layers, increasing the specific surface area and sorptive capacity. The use of 'activated' clay minerals in skin-care products continues to be an area of active research. As an example, activated bentonite was included in electrospun nanofibers (Bazbouz & Russell, 2018) to prepare a product with skin-protection properties. A mineral-based sunscreen containing activated clay combined with a dispersing agent and one or more inorganic sunscreen actives has been patented. As a result, a mineral sunscreen with

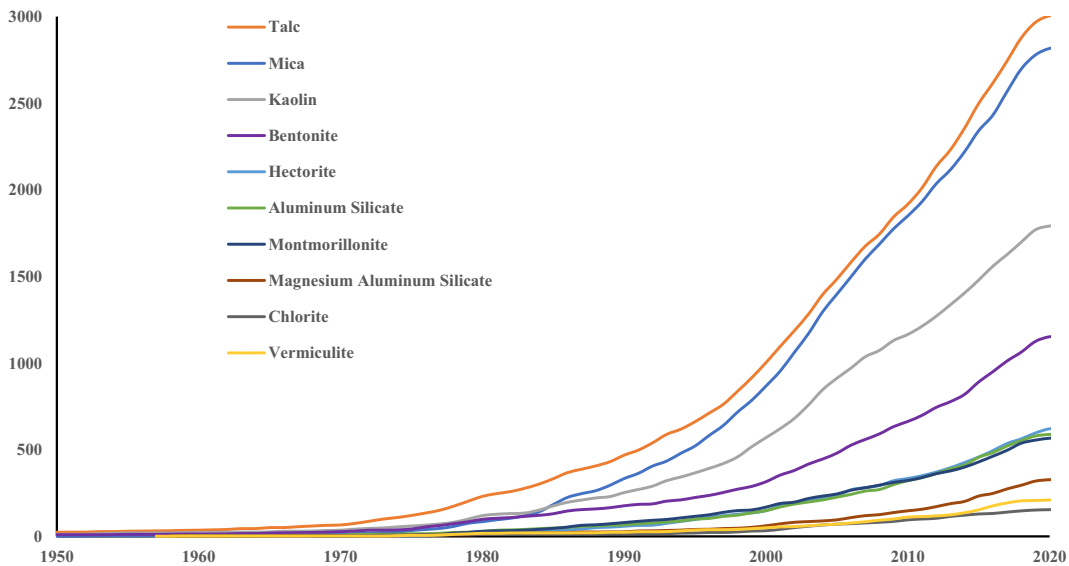

Fig. 4. Trends in terms of the top ten INCI clays included in the patent applications for cosmetics (over the period 1950–2020)

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Table 3. Smectites used as cosmetic ingredients

Group	Minerals	INCI name	Description	Functions
Dioctahedral smectites	Hectorite	Hectorite	-	Absorbent, bulking, viscosity-controlling
	Modified hectorite	Dihydrogenated tallow benzylmonium hectorite *	Quaternary ammonium compounds, benzylbis (hydrogenated tallow alkyl) methyl, salts with montmorillonite	Antistatic, gel forming, viscosity-controlling
		Disteardimonium hectorite	1-Octadecanaminium, N,N-dimethyl-N-octadecyl-, chloride, reaction products with hectorite	Light stabilizer, viscosity-controlling
		Quaternium-18 hectorite	Quaternary ammonium compounds, bis (hydrogenated tallow alkyl) dimethyl, chlorides, compounds with hectorite	Viscosity-controlling
		Stearalkonium hectorite	Benzenemethanaminium, N,N-dimethyl-N-octadecyl-, chloride, reaction products with hectorite/Quaternary ammonium compounds, benzyl (hydrogenated tallow alkyl) dimethyl, chlorides, compounds. with hectorite	Gel-forming, viscosity-controlling
	Saponite	-	-	Absorbent, hair-cleaning
	Stevensite	Moroccan lava clay	-	Absorbent, hair-cleaning
Trioctahedral smectites	Montmorillonite	Bentonite	A colloidal clay. Consists primarily of montmorillonite	Absorbent, bulking, emulsion stabilizing, viscosity-controlling
		Montmorillonite	Montmorillonite	Absorbent, emulsion stabilizing, light stabilizer, viscosity-controlling
		Hydrogenated tallowalkonium bentonite	The product of the reaction of hydrogenated tallowalkonium chloride and bentonite	Viscosity-controlling
		Quaternium-18 bentonite	Quaternary ammonium compounds, bis (hydrogenated tallow alkyl) dimethyl, salts with bentonite	Viscosity-controlling
		Quaternium-18/benzalkonium bentonite	Quaternary ammonium compounds, bis (hydrogenated tallow alkyl) dimethyl, compounds with bentonite and C8-C18-alkylbenzyldimethylammonium chloride	Viscosity-controlling
		Quaternium-90 bentonite	A reaction product of bentonite and quaternium-90	Viscosity-controlling
		Stearalkonium bentonite	Benzenemethanaminium, N,N-dimethyl-N-octadecyl-, reaction products with bentonite	Gel-forming, viscosity-controlling
		Benzalkonium montmorillonite	The reaction product of benzalkonium chloride and montmorillonite	Surfactant-emulsifying, viscosity-controlling
		Quaternium-90 montmorillonite	The product obtained by the reaction of quaternium-90 and montmorillonite.	Surfactant-emulsifying, viscosity-controlling
		PVP montmorillonite	Montmorillonite surface treated with 2-pyrrolidinone, 1-ethenyl-, homopolymer	Emulsion-stabilizing, film-forming, viscosity-controlling
	Beidellite	-	-	Absorbent, emulsion-stabilizing, light stabilizer, viscosity-controlling
	Nontronite	-	-	Absorbent, emulsion-stabilizing, light stabilizer, viscosity-controlling

Table 3. (continued)

Group	Minerals	INCI name	Description	Functions
Non specified smectites	-	Argilla	Naturally-occurring substances. Smectite group minerals	Abrasive, bulking humectant
	-	Argilla extract	Smectite group minerals, clays, extract	Skin-conditioning
	-	Magnesium aluminum silicate	-	Absorbent, anticaking, opacifying, viscosity-controlling
	-	Tromethamine magnesium aluminum silicate	Smectite-group minerals, products with 2-amino-2-hydroxymethyl-1,3-propanediol	Viscosity-controlling

*The hydrogenated tallow fatty radicals are derived from tallow fatty acids, including oleic (~40%), palmitic (~25%), stearic (~20%), myristic (~5%), and linoleic (~2%) acids with other minor components.

high UVB/UVA protection, non-whitening effect, and exceptional spreadability was obtained (Timothy et al., 2015). An emulsion with unspecified phyllosilicates together with "inosilicate, cyclosilicate, tectosilicate, neosilicate, or sorosilicate" have been used as skin-care products (Rochette et al., 2017).

Traditional and historical provenance names are included as cosmetic ingredients: Canadian colloidal clay, Elguea clay, Heilmoor thermal clay, and Palau white clay. Canadian colloidal clay is used as skin conditioning in cosmetic formulations. The commercial mask, Gravitymud© (Estee Lauder®), contains Canadian colloidal clay. Many of these clay materials are used in thermal centers to prepare suspensions with mineral waters (referred to as peloids or thermal muds). Because the majority are not commercialized, it is difficult to determine their composition, stability, and properties (Sánchez-Espejo et al., 2014). Together, some of these clay materials are sold without quality control, e.g. Medina Clays (Khiari et al., 2014).

The following list of references provides access to detailed information on the use of clays in pelotherapy (Veniale et al., 2007; Gomes et al., 2013; Carretero, 2020a, 2020b). Some examples of commercialized peloids are Elguea and Heilmoor clay. The Elguea clay is a native clay obtained from Elguea Cuban thermal center (Villa Clara province), known for its abrasive and absorbent properties. The peloid used in this thermal center has a hydrothermal origin and a dark gray color. It is composed mainly of clay minerals, carbonates, and halite (Rizo et al., 2017, 2018). Heilmoor clay (trade name: Thermal Heilmoor© clay) is a natural mud from Heilmoor (Austria), formed slowly by the accumulation and decomposition of vegetal residues at the bottom of peat bogs. Its ability to improve blood circulation and the presence of numerous organic and inorganic components able to partially penetrate the skin make the mud an optimal ingredient for cosmetic products with revitalizing and purifying properties. Face mask with propolis for oily skin (Apivita® Company) is a commercial cosmetic that includes Heilmoor© clay as an ingredient. Palau white clay is obtained from Ngeruktabel Island in Palau (western part of the Pacific Ocean). The Hokkaido Akan© clay is obtained from the volcanic area of Hokkaido Akan Caldera, Japan. The basement of Akan volcano consists of Cretaceous–Tertiary sedimentary and volcanic rocks. Manicouagan clay© is located in Baie-saint-Ludger, in the Manicouagan peninsula. Argile Eau Mer® is the company responsible for exploiting this clay and for the manufacture of three types of products for cosmetic and therapeutic applications. Detox shampoo© by American Crew® includes Manicouagan© clay among other ingredients.

CLAYS IN COMMERCIAL FORMULATIONS

Cosmetics formulations may contain more than one clay among their ingredients. A considerable number of cosmetics exist that include clays as ingredients; examples are listed in Table 7. Some clays are used for their technological functions and others for a specific cosmetic function, e.g. cosmetic formulations with halloysite, kaolinite, and montmorillonite

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allow 5–10 wt.% loading efficiency and 10–20 h of sustained release of glycerol, ascorbic acid, and other bioactive compounds (e.g. vitamins) (Suh et al., 2011). Cosmetic patents often propose alternative clay minerals for the same functions. For instance, a composition with a UV-shielding effect included microparticulate titanium dioxide, magnesium, and/or calcium hydroxide and a clay mineral that could be selected from mica, talc, kaolin, bentonite, or smectite (Ijiri et al., 2015).

CONCLUSIONS

Clays are used in numerous cosmetic formulations with both technological and cosmetological functions. The trends, since 1950, of the top ten clays (INCI names) in patent applications for cosmetics are shown in Table 4. Talc, kaolin, mica, and smectites are the clay minerals used most frequently in cosmetic products, with a sustained increase in their use, followed by other clay minerals. As with other industries, controversies exist about the use of certain names to refer to materials, which makes understanding difficult and which should be standardized. The current study has summarized and highlighted the possibilities offered by clays and clay minerals in the cosmetics field. The cosmetic ingredients and final cosmetic product markets are concentrated in a few companies. New, advanced uses of clays could open the market to include novel companies in this market in the future Fig. 4.

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Declarations

Conflict of Interest

The authors declare that they have no conflict of interest.

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