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Silicone emulsions Interfacial aspects and applications

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ABSTRACT: Silicone polymers are a class of hybrid organic/inorganic polymers, that show desirable surface properties such a low surface energy and high flexibility, which enables even a very high molecular weight chain to achieve optimal orientation at the interface. Silicone polymers have dual characteristics, because of which they can either be used as emulsifiers or act as the continuous/dispersed phase of the emulsion in presence of surface active agents. Major characteristics of silicone emulsions are discussed in this review along with new information on silicone surfactants used for emulsification. Finally an analysis of silicone emulsification technology is presented along with their recent applications and significance to the modern day life style.

INTRODUCTION

Emulsions are a dispersion of one liquid in another, which are not miscible and will slowly separate into separate phases if mixed (1). One of the liquid phases is water and the other a water-insoluble organic liquid, which is generally oil. Emulsions are macro- or micro-sized dispersion of one liquid in another, most commonly an oil-in-water or water-in-oil. Emulsions are used in diverse applications ranging from cosmetics and personal care (2) to paints/textile/polishes (3) and drugs (4). Emulsion technology involves creating emulsion, through the use of droplet stabilizing agents including surfactants, which will allow emulsion life span sufficient for its desired application. Thus, in most practical applications, emulsions are defined in terms of their usable life. Such usable life may vary from few months to years depending upon the specific application. Some emulsion applications require relatively stable formulations during storage and its destabilization during its actual application. Micro emulsions, with droplets of 20 - 100 nm size range are thermodynamically stable dispersions within the defined boundary conditions of concentrations, pressure and temperature. They are created by the addition of a third phase, which could be a surfactant which creates compatible interfacial conditions thereby allowing two primary phases to be in the dispersed state in contact with each other. The key in this case is to create interfaces of ultra low interfacial energies between the two phases in question, which otherwise would have appreciable interfacial energy (5). This review focuses on a subclass of emulsions, namely silicone emulsions and their applications, but it would be appropriate to discuss the underlying concepts of emulsion formation before delving into the details of silicone based systems.

Discussion on HLB

The type of emulsion obtained using a non-ionic surfactant is determined by the proportions of the hydrophobic and hydrophilic parts of the surfactant as is described by Hydrophile-Lipophile-Balance (HLB) value which increases with the polarity of the molecule (6-8).

The geometry of the micelle and hence the encapsulated emulsion droplet can be represented by structure parameter P,

$$P = \frac{v}{a_0 l_c}$$

where v is the volume of the surfactant molecule, a₀ is the area of the surfactant head group and l_c is the length of the surfactant molecule.

Surfactants with P = 1/3 give cone shaped molecules, surfactants with P=1/2 gives slightly cone shaped molecules. When P=1, molecule of cylindrical shape are obtained and when P>1, reverse cone shaped molecules are obtained.

Direct application of conventional HLB concept for choosing an emulsifier in conjunction with silicone surfactants often results in misleading HLB values due to the fact that silicones are organic/inorganic hybrids and hence fall neither into the conventional categories of hydrophilic or hydrophobic. Moreover, prediction of the HLB and emulsification properties of blends of silicone and hydrocarbon surfactants is an additional challenge. The



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difficulties mentioned above have led to the development of a concept called "3 dimensional HLB", an approach first developed by O'Lenick et al. (9). This empirical system is an extension of the HLB concept, and it is so named because it includes contributions from the three components related to portions of the molecule that are soluble in either silicone, oil or water.

The general stability of an emulsion process can be related to the rate-of-the breakdown processes, which occur sequentially by the molecular diffusion of the dispersed phase through the continuous phase. The rate of breakdown results in a decrease in the free energy (10) which in turn depends on the following parameters (5).

1. physical nature of the interfacial film
2. existence of an electrical or steric barrier on the droplets
3. viscosity of the continuous phase
4. size distribution of the droplets
5. temperature
6. density of the two phases

SILICONE EMULSION

Silicone (e.g. poly(dimethyl siloxane) and derivatives) polymers are an important class of hybrid organic/inorganic polymers that have been commercialized extensively in their liquid state. Silicones differ considerably from their organic counterparts due to their weak intermolecular attractive forces. Structurally they are characterized by 1) Si-O-Si bond angles (140°) that are larger than C-O-C bond angles (110°), 2) Si-O bond lengths (1.64 Å) that are longer than C-C bonds (1.53 Å), 3) a greater freedom of rotation around the Si-O bond compared to the C-C bond and 4) freely rotating methyl groups which can orient towards interfaces (11). These characteristics allow silicone molecules to present it in unique molecular configurations that allow lower interfacial energies and outstanding lubricating properties at low pressures. Silicones are water repellent, heat stable, and highly resistant to chemical attack (11). Since silicones are insoluble in both water and many hydrocarbons, a very common mode of delivering them is in the form of emulsions. The delivery of silicones in hydrocarbons or hydrocarbon continuous emulsions has gained little interest; therefore only water-continuous emulsions will be considered in this paper. Silicone emulsions typically contain water, silicone oil, stabilizing surfactants, preservatives and other additives for viscosity stabilization and freeze-thaw stability (5). The low surface tension and incompatibility of silicones with water and many hydrocarbons pose unique problems that make emulsification process distinctly different from traditional hydrocarbon emulsification processes (8). Thus most surfactants that are considered suitable for emulsification of hydrocarbons and fats are not effective for silicones. Additionally, chemical modifications of silicones further complicate the emulsification technology for silicones. Although any type of surfactants could be used to develop silicone emulsions, majority of emulsions involves the use of non ionic surfactants (6).

SILICONE EMULSION CLASSIFICATION

Based on emulsion type, the silicone emulsions can be classified as:

- a. Macro-emulsions - They are the most common type of

emulsions with a droplet size in the range of 0.3 – 1.0 micron. They are also called mechanical emulsion, as they are prepared through the mechanical process of intense mixing (12). Visually opaque but the individual droplets can be easily observed under a microscope. Macro-emulsions are thermodynamically unstable, but are kinetically stabilized using surface active agents, and viscosity enhancers. This is the most common form of silicone emulsions and is used in mold release, polishes, antifoams, personal care, food, drugs etc.

- b. Mono-dispersed-emulsions - They are blue-white type emulsions with particle size range in between 100nm to 400nm and are formulated through emulsion polymerization process. These are primarily in a narrow droplet size range, often +/- 1.5 units. Major applications of these emulsions are in hair care, personal care and home care industry.

- c. Micro-emulsions - They are transparent and the most stable form of emulsions in which the particle size ranges from several 10 nm to 100nm. They are thermodynamically stable and are manufactured by careful choice of surfactants and moderate mixing. Major use of these emulsions is in textile and personal care industries (13). Micro-emulsion is characterized by its clarity, transparency and particle size.

EMULSION STABILIZATION

Silicone emulsion stabilization is achieved through the use of surfactants. The goal is to decrease interfacial tension between the fluid/water interface and disperse the droplets to eliminate flocculation or coagulation. Due to compatibility issues, non-ionic surfactants are the preferred choice of surfactants for this emulsification process, although in some of the applications, anionic surfactants are used. Even though in the past, majority of surfactants used were organic surfactants extended from organic emulsification processes, there is a drive to shift to silicone surfactants to produce new generation of emulsions. As such the industry has evolved through the extension of organic fluid emulsification technology to silicone fluids. The approach has been to select/modify traditional surfactants and utilize them to develop silicone emulsions. While non-ionic surfactants such as nonyl phenol ethoxylate do stabilize emulsions based on entropic steric effects, in many instances, pH has been used to create ionic repulsions to stabilize droplets and achieve ultralow interfacial tensions (14). Specifically, in the micro-emulsification of amino modified emulsions, use of acetic acid (pH 4 – 6) do create surface charge on amine groups there by adding a new dimension to such fluid stabilization.

Through organic surfactants

Nonyl phenol ethoxylates, dodecyl alcohol ethoxylate and tridecyl alcohol ethoxylates are the most common surfactants used to manufacture non ionic fluid emulsions at about 7-8 percent of the fluid used (14,16). Additionally, fatty acid esters such as sorbitol mono - stearates, - oleates and similar esters are also used to manufacture emulsions. While most of the fluids emulsions are stabilized at pH 6.5 – 7.5, many of the amino emulsions are stabilized in micro-emulsion form at 4.5 – 6 pH range. Anionic emulsions are stabilized using dodecyl sulfonic acid at concentrations of 8-10 percent of the fluids used.

Silicone oils can often be emulsified by hydrocarbon surfactants also, where the silicone polymer acts as the oil phase instead of being the surfactant. Poly(dimethyl

siloxane) (PDMS) oils are widely used in the industry for controlled release (15), foam control agents, lubricants, fabric treatment (16) and base fluids in a number of products like cosmetics and polishes. In spite of this very little has been published in the open literature. Binks et al. (17) has investigated several aspects of the emulsion and equilibrium phase behaviour of mixtures of water, non-ionic

surfactant (C_nE_m) and silicone oil (PDMS). Emulsions were inverted from oil-in-water to water-in-oil by increasing the temperature or the concentration of NaCl electrolyte. The apparent phase inversion temperature (PIT) increased with an increase in the number of oxyethylene groups in the surfactant (E_m), and decreased with an increase in the surfactant alkyl chain length (C_n). The PIT also decreased when NaCl was added but increased in the presence of tetrabutylammonium bromide as electrolyte. Purohit et al.

(16) have studied the interactions of functionalized silicones with various fabric substrates in order to understand the underlying mechanisms of interactions. In this study modified amino silicones were emulsified using non-ionic surfactants (lauryl and nonylphenol ethoxylates) to form oil-in-water emulsions. These emulsions act as delivery agents for the silicone droplets, which impart the desired physical properties to the fabric substrates. They are stabilized by excess surfactant (usually 20-25 percent) since during the actual application they are diluted to a great extent. The electrokinetic properties of the emulsions were monitored in this study since charge plays an important role in the interaction with the fabric substrates. Around pH 8 there is a sharp fall in the zeta potential with the isoelectric point being in the range of pH 9-10 for the four different modified emulsions. Due to the quaternization of amino groups by dimethyl sulphate the zeta potential was expected to demonstrate a steady positive behaviour and the quaternized groups were expected to be stable in all pH range. It was also observed (16) that the emulsions turned hazy at alkaline pH (pH 8 – 10). This behaviour is noteworthy since this is the range in which commercial operations run into difficulties. Nephelometric analysis showed a sharp increase in turbidity in the pH range of 9-10 where electrokinetic behaviour also changed sharply and this was attributed to the breaking of the emulsions (16).

Through silicone surfactants

Silicone emulsifiers can be polymeric or oligomeric and can possess one or more hydrophilic functional groups (3). Moreover the nature of functional groups can be ionic or non-ionic. In contrast to low-molecular-weight surfactants, multifunctional polymeric emulsifiers can attach to an interface via several segments. The energy of adsorption is equal to the sum of the interactions of all segments, and can be considerably greater than the energy of individual monomeric surfactants. Hence these multifunctional

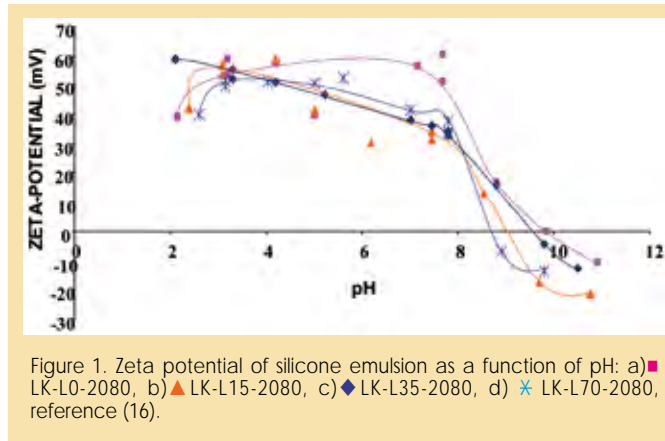


Figure 1. Zeta potential of silicone emulsion as a function of pH: a) \blacksquare LK-L0-2080, b) \blacktriangle LK-L15-2080, c) \blacklozenge LK-L35-2080, d) \times LK-L70-2080, reference (16).

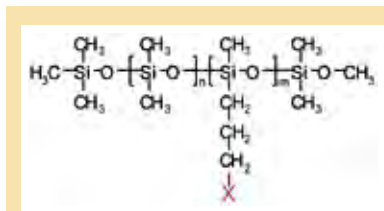


Figure 2. General structure of silicone surfactant. X represents hydrophilic modification such as amino (-RNH₂); carboxy (-COOH); epoxy (CH₂CHO) or poly alkoxy (EO/PO). For monomeric surfactant, n=0 and m=1.

as silicone copolyols) have been studied for their emulsifying properties in some detail (11). In most cases, the hydrophilic moiety of choice has been poly(oxyethylene) (EO groups) because of its good water solubility and ease of synthesis with a wide range of molecular weights. Such emulsions are widely used in the cosmetics industry as either antiperspirants or creams for skin care and sun protection. In addition to linear silicones, cyclic silicones are also employed in industry due to their special volatile character. There has been some work done on the phase diagrams of cyclic silicone oils (D_4 , D_5) and linear silicone chains, mixed with water and non-ionic silicone surfactants (18, 19). These phase diagrams show a variety of regions including simple micellar solutions (L1 and L2), microemulsions, and liquid crystalline phases. A detailed discussion on various systems and the temperature dependence of such surfactants is given elsewhere (22). Although non-ionic surfactants are very effective in lowering interfacial tensions of aqueous systems, they are not very tolerant of pH variations and tend to hydrolyze to long chain alcohols. Since long chain alcohols are irritants, non-ionic silicone surfactants are not suitable for use under all pH conditions. Moreover, a very long chain of polyethylene oxide and/or polypropylene oxide is often needed to make a non-ionic silicone water-soluble.

polymeric emulsifiers can adsorb very strongly at an interface. They can be used in low dosages and are very efficient in generating highly stable emulsions. Polymers neither readily desorb from an interface, nor migrate through the bulk phase because of their strong adsorption at the interface.

Silicone polymers comprising a non-ionic hydrophilic group and a hydrophobic poly(dimethyl siloxane) chain (also known

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Therefore for a given weight of non-ionic silicone surfactant, the silicone fraction is usually much reduced. Some of the disadvantages of silicone copolyols can be avoided by using ionic silicone surfactants. Somasundaran et al. (20) have evaluated the emulsifying ability of several anionic, cationic and amphoterically modified silicone polymers. Results show that the anionically modified silicone polymer stabilizes an emulsion of water in cyclic silicone oil (D_5) but interestingly in a narrow window around composition of 80 percent water and 20 percent oil. The phase diagram is shown in Figure 3. It was observed that 80 percent water was stabilized as an inverse emulsion in 20 percent of the oil phase. The droplets were relatively large ranging to tens of microns. It is noted that, these concentrated macro-emulsions were stable for weeks even with just 0.2 percent surfactant.

Ternary emulsion systems

Ternary emulsions, often termed double emulsions, are complex liquid dispersion systems known also as "emulsion of emulsion", where the droplets of one liquid dispersion are further dispersed in another liquid (20). The inner dispersed droplets in the double emulsions are separated (compartmentalized) from the outer liquid phase by a layer of another phase (21). Usually the size of the droplets of the inner emulsion is small ($1\mu\text{m}$ or less) while the size of the outer emulsion globules can be significantly larger ($20\text{-}100\mu\text{m}$). These types of emulsions are particularly important when protection of a sensor attribute of the internal phase is required (22).

Polymeric surfactants are typically chosen to stabilize such emulsion systems because they adsorb at the interface more strongly than monomeric surfactants. Macromolecular surfactants have the advantage of attaching to a surface via several segments. Even if the free energy of adsorption per segment is low, the attachment of several segments leads to a large total free energy of adsorption. As a result, their adsorption onto surfaces is less reversible and they can be used efficiently even at lower concentrations. Polymers can stabilize the droplets via both steric and depletion stabilization mechanisms (23). Polysiloxanes grafted with non-ionic poly(ethylene oxide) moieties have proven to be excellent steric stabilizers for this kind of emulsion (24). The high emulsifying power of silicone-derived polymers, their strong adsorption to the W/O interface and the pronounced elasticity of the interfacial film, are the basis for the stability

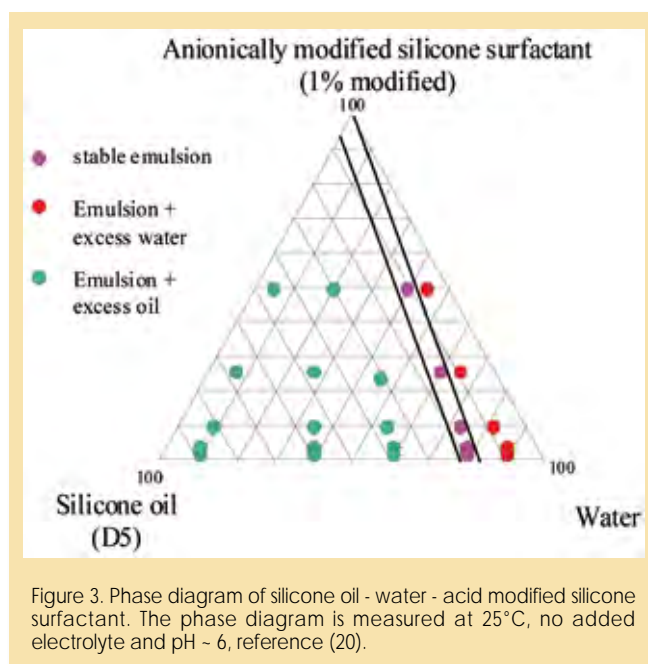


Figure 3. Phase diagram of silicone oil - water - acid modified silicone surfactant. The phase diagram is measured at 25°C , no added electrolyte and $\text{pH} \sim 6$, reference (20).

of double emulsions with silicones (22). Few commercial applications of double emulsions are known and this can be attributed to their thermodynamic instability and the uncontrolled, fast release of entrapped materials such as electrolytes or other dispersed materials. These emulsions are potential systems for sustained and slow release with possible applications in the areas of pharmaceuticals, enzyme fixation, cosmetics and agriculture (22, 25). Such emulsions can also develop high viscosity, which is desired in cosmetic applications for creams and lotions.

APPLICATIONS

Some of the key applications of silicone emulsion systems are discussed below.

Personal care industry

Silicone emulsions for personal care appears either in the form of antiperspirant formulations or creams and lotions for skin care and sun protection (13, 14). These are mostly water-in-silicone-oil emulsions that possess the special properties of silicones: excellent spreading and film-

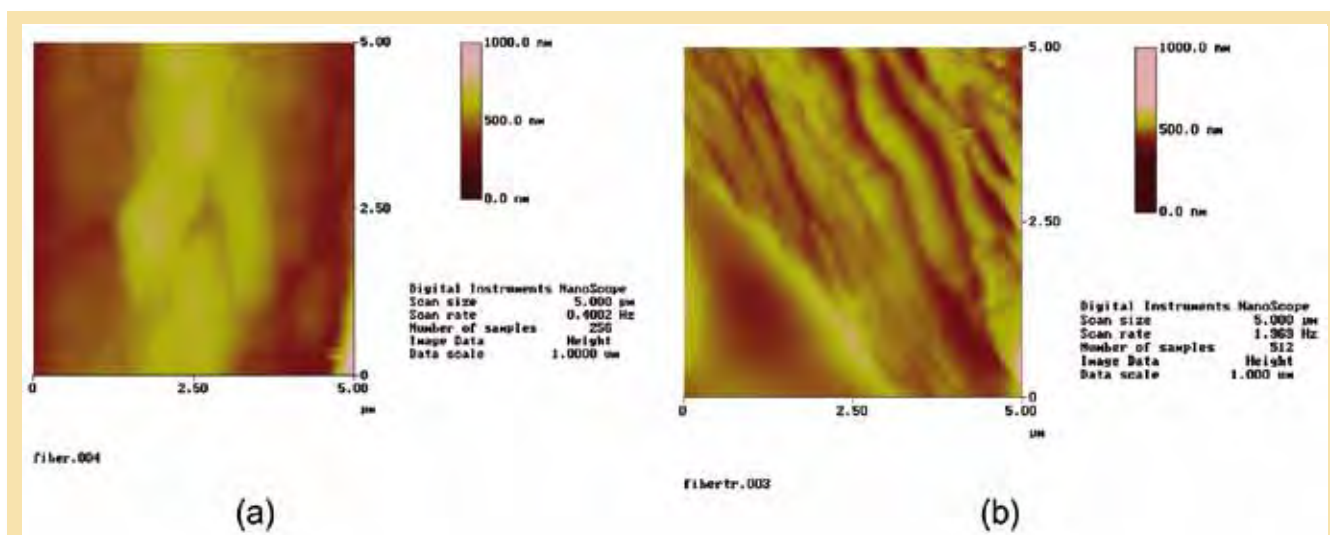


Figure 4. AFM images of (a) untreated fabric, (b) treated fabric., reference (16).

forming properties, gloss, dry nonsticky feel (22). Antiperspirants contain concentrated aqueous aluminum chlorohydrate emulsified in cyclic dimethylsiloxanes for easily applied formulations. The siloxanes facilitate application, reduce the stickiness of chlorohydrate and evaporate without giving a chill effect. Polish formulations in the form of water-in-silicone emulsions are obtained in a way similar to those described for antiperspirants. Silicones in these applications create easily spreading films and also facilitate the transport of other polishing oils and waxes. Typically these polishes contain abrasive materials in the water phase and in addition to silicone fluid, other solvents like mineral oil and alcohols are included in the oil phase.

Textile industry

Fabrics and other such materials undergo finishing operations with surface active materials to impart desired surface properties. Silicones have been used as premium finishing agents because they offer durable, longer lasting surface modifications to the fabric (26, 27). Surface and bulk characteristics of fabrics such as softness (surface or inner), bounciness, tear strength, dry feel, wet feel, hydrophobicity, hydrophilicity and several other fabric properties can be enhanced significantly by modifying silicones for desired transport and interfacial properties. These silicones are applied to the fabric surfaces as micro- or macro-emulsions. In the actual process, micro- or macro-droplets of silicone are adsorbed onto the fabric surface leading to its surface modification.

Purohit et al. have studied the morphology of fibres using AFM in order to determine the manner in which the surface treatment alters their surface properties (16). It can be seen from the figures below that the treated fibre is more uniform, well stacked, and relaxed compared to the untreated fibre. Also it appears that a single fibre structure is divided into many fibres after the silicone treatment. This indicates that the silicone treatment is responsible for changes in the micro properties of the fibres, and can be used to modify microstructural properties of fibres to induce smoothness, bounciness and other such desirable properties in the fabric.

Other applications

Silicone oils and emulsions are used as lubricants and release agents in a variety of fields (28). Various silicone emulsions are used as release agents for manufacturing rubberized belts, lubricants to prevent wear and increased abrasion resistance to latex rubber, as release agents in the printing industry, as lubricants for yarn and sewing threads to eliminate friction and tension, and as finishes to improve water-repellency and scuff resistance for leather, vinyl and foam upholstery. In an interesting application silicone emulsions have been used as lubricants in pea-seed protectants (28).

Silicone emulsions have been employed to treat glass surfaces in order to add new advantageous properties such as the removal of a water film, lowering the wettability towards water, and increase of the tensile strength. Advantages of lowered wettability of glass by silicone treatment in the pharmaceutical area include: 1) retardation of blood coagulation; 2) complete emptying of medicines from bottles. In the drilling of oil wells, the drilling fluids used can be brine-in-oil emulsions, which must be stable at high temperatures and pressures. Calcium chloride, calcium bromide or zinc bromide are used to obtain brines with high specific gravity to improve the pressure control. These conditions require emulsifiers of high performance, which is the case for silicone-based

emulsifiers (29). In a similar application silicone emulsions of lower viscosity have been used for removal of chlorinated solvents from contaminated subsurface environments (30).

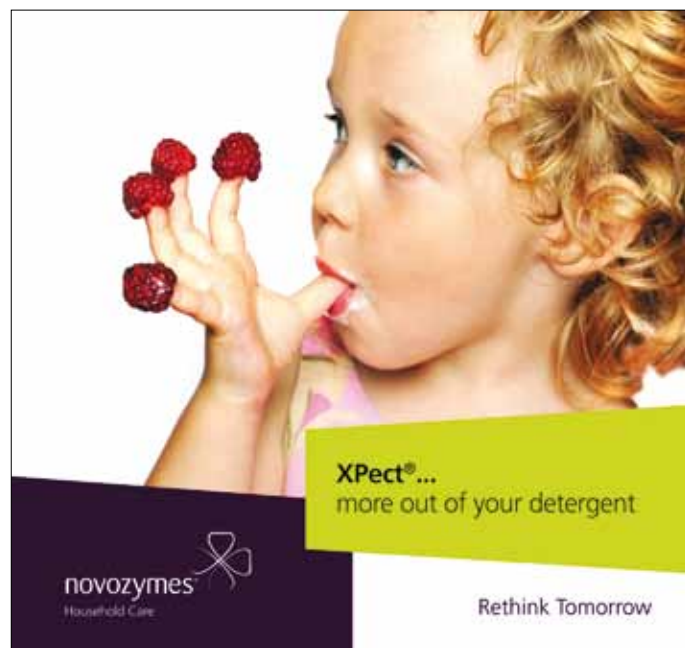
CONCLUDING REMARKS AND FUTURE DEVELOPMENTS

The market for drug delivery technologies has been expanding over the last few decades with the developing countries providing quality health-care to their huge populations. For example, a rapidly growing segment of this market is transmucosal and transdermal delivery technologies (31). As the drug molecules lose patent protection, pharmaceutical manufacturers look for methods to extend product lifecycles. Novel delivery methods can provide this extension. In this regard, silicones are combined with various pharmaceutical agents as antibiotics, antidepressants, anxiolytics, antifungals, antivirals, analgesics, and selected vitamins (32, 33). With zero order release rates, many of these pharmaceutical infused silicones can release 10 to 500 micrograms of agent per day.

Silicone emulsions possess intriguing properties such as stabilization of as much as 80 percent water in inverse emulsion form and are thus a subject of fundamental interest. Silicones depict some specialty applications, such as stabilization of polyurethane foams, which none other hydrocarbon surfactants can cause. Because of such properties, even though relatively more expensive than the hydrocarbons, silicones are widely commercialized. Silicones are used in the form of binary as well as ternary emulsions and can be oil or an emulsifier. Polymeric silicones (polydimethyl siloxanes and amino-modified polydimethylsiloxanes) as well as cyclic silicones are mainly used as silicone oils in emulsions. Some of the important applications of silicone emulsions are reviewed in the paper. It is clear that silicones offer opportunities to produce new materials with unique properties at relatively low cost.

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HOMAGE TO...

Roberto Franchina and Framesi - Today as a reminder of yesterday

Roberto Franchina, founder of Framesi, passed away in July, aged 87.

Roberto Franchina founded Framesi (the name comes from the initials of his and the shareholders' names, Messa and Sironi, whose shares Franchina will acquire shortly after the company's incorporation) at a very particular time, the post-war years in Italy, a devastated country anxious for redemption and to lay the path for a brilliant future.

At the time, the company sold professional hairstyling products. Those who recall those years are aware how different barber and hairdresser shops were compared to today's hairdressing salons, where hair now plays a key role in beauty care for men and women alike. If so dramatic changes have occurred, if going to the hairdresser today is not simply to have your hair cut, much part of the change we owe it to the work of Roberto Franchina, who at a certain point understands that hair beauty is something very closely related to the looks of a person, thus varies according to fashion trends, changes to cultures and society. This revolution is started in the 1970s, and not at all by chance. In those years, people's habits and ways of life were changing dramatically, and so were fashion trends. Nothing was given for granted any longer, the world started revolving at a much faster pace, unknown until then. New desires, demands and needs rapidly develop and involve the very person, and the way one looks. Framesi grew rapidly and so did its production and trade relations, with relationships expanding throughout the world, and the rapid development of the company's research and training activities.

Today, Framesi provides beauty salons with means and resources to offer both quality products and advice to end users, be they men or women. It is all about building that professional attitude that is centered on providing a quality service to the beauty salon customers, making them feel protagonists of their own looks and well being. Roberto Franchina has achieved all this through strength and endurance. He was 23 when he first started, a true example of professionalism to any young person, an entrepreneur with an incredibly strong personality. We have collected feedback describing how much Roberto Franchina was close to his business, got involved in the day to day work and was always next to his employees, whom he treated as a family.

Today the company is led by his sons: Fabio, the company's president, and Roberta, the general manager. Recently, Fabio Franchina, former president of Unipro, was appointed COLIPA chairman. It is a much deserved and prestigious achievement and recognition of his work, even more significant for the Franchinas in this moment of grief for the beloved father. As it has always been, an Italian entrepreneur is again leading a company that has led the markets worldwide, through professionalism and commitment, taking the so very much well regarded, and at times even envied, "Made in Italy" brand to the world. Undoubtedly, Framesi will continue to be regarded as a reference, a true example of success in the cosmetic business.

Framesi has and will be a wonderful business venture to tell about, ever so important today, where we face new challenges and the pace of the world has sped up dramatically, because it shows that everything is possible if we passionately throw ourselves into what we believe in.

This is exactly the sense of our memories on Roberto Franchina today.