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Microencapsulated Fragrances in Melamine Formaldehyde Resins

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Abstract: The process for making melamine formaldehyde microcapsules containing fragrant oil is well-known. Recently, this technology has been used to enhance the olfactory performance on fabrics. However keeping the fragrance in the capsule during storage, improving the olfactory benefit and releasing a low amount of formaldehyde is highly challenging. To answer these challenges, Givaudan has developed its own melamine formaldehyde microcapsule, called Mechacaps™, which is described in this article.

Keywords: Controlled release · Fragrance · Melamine formaldehyde · Microcapsule · Thermoset resin

1. Context

Historically, carbonless copy paper, launched by National Cash Register[1] was the first microcapsule application on the market. When pressure is applied by writing, the capsules break and the dye is released onto a paper containing acidic clay which renders the dye visible. Microcapsules were made by complex coacervation of gelatine with Arabic gum.

Since this first application, microcapsules have been introduced in many other industries. In agriculture, encapsulated pesticides are released over time.[2] These products are not only more active gram for gram but also safer to both operators and the environment. In food, microencapsulation is used for taste masking but also to protect flavors from their external environment.[3] In fine fragrances, the scratch and sniff technology has become a standard in advertising.

In 1999, Dim was the first company to launch fabrics with microcapsules grafted on textile fibers. The idea was to give a cosmetic effect (moisturizer in this case) to a textile fabric. It was the birth of a new specialty called cosmeto-textiles which made a success of companies such as Outlast[4] who associated phase-change material in a permanent way with textile fabrics to make thermo-regulating clothes.

Beyond driving the impression of cleanliness on fabrics, fragrance is directly linked to our emotions, memory and way of life.

The fragrance diffusion on dry cloth is perceived as a quality criterion for consumers. In classical perfumery, the olfactory performance is quickly lost during drying after the wash. Our objective was to deliver the overall same high level of olfactory performance during the entire product life as shown in Fig. 1.

Inspired by the first cosmeto-textile successes, microencapsulation[5] of the fragrance in a polymeric shell appeared to be the best technology to reach this target. The role of microcapsules is:

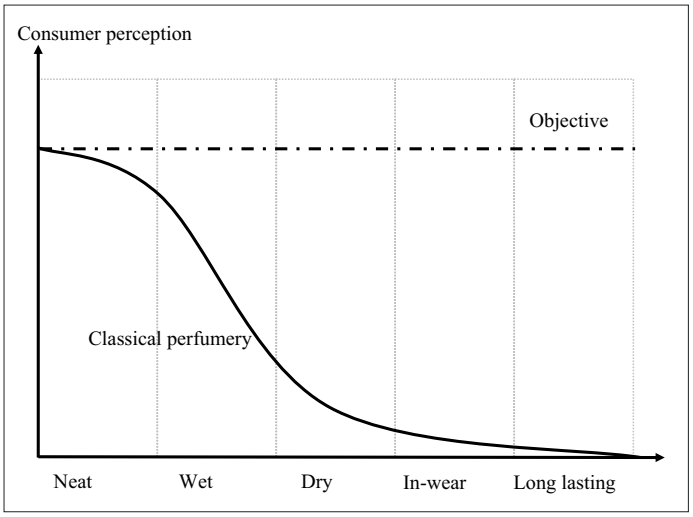

Fig. 1. Difference between classical release profile and performance expected by consumers.

- to capture the fragrance/accord in its original form with minimum change and maximum retention;
- to protect the fragrance from uncontrolled interaction with the environment and from premature release during storage;
- to completely release the fragrance where and when it is desired.

Due to obvious technical constraints, encapsulating fragrances and keeping them inside microcapsules during storage in commercial bases is highly challenging. In the cosmeto-textile field, mainly inert or high molecular weight compounds are encapsulated. As fragrances are mixtures of low molecular weight and often reactive raw materials, they can disturb the microcapsule process or diffuse easily through the microcapsule shell.

Givaudan developed its own microencapsulation technology, called Mechacaps™, based on aminoplasts which is described in this article.

In 2006, melamine formaldehyde microcapsules[6] were launched for the first time in a fabric softener base. Fresh and fruity notes could be perceived after 14 days on dry fabrics for the first time ever.

2. State of the Art

A popular and convenient method for producing encapsulated formulations consists in dispersing the ingredient (oil phase to be encapsulated) in a liquid and creating a polymeric membrane at the surface of the oil droplets. Many polymers or mixtures of polymers capable of forming insoluble complexes under specific conditions can be used to form interfacial membranes by the so-called polymer phase separation process.[7]

Interfacial membranes can be produced by the polycondensation of various co-monomers and macromonomers. The polycondensation of urea with formaldehyde (UF), melamine (2,4,6-triamino-1,3,5-triazine) with formaldehyde (MF) to form so-called aminoplast microcapsules is the most popular among these pro-

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cesses, leading to shells consisting of highly cross-linked resins (also known as thermoset resin).

The use of melamine to encapsulate hydrophobic materials in water was first published in 1969.[8] Then, melamine formaldehyde resins were used in pigments[9] and inks.[10] The use of protective colloids[11,12] able to improve microcapsule performance and stability was patented by BASF in the eighties.

In the nineties, collaboration occurred between P&G[13] and 3M. The aim was to use these microcapsule types in consumer products, without any launch on the market. These capsules were described to be relatively stable in softeners but were in need of a hard rub to release the encapsulated fragrance.

In 2005, IFF patented capsules[14] with a heavy solvent and a sacrificial solvent which was exchanged with the non-encapsulated perfume when the capsule was introduced in softener. More than 70% of the fragrance is retained after a week. The microcapsule stability[15] was claimed to be highly improved by heating the slurry at higher temperatures.

Despite all these improvements, three main challenges were still unsolved:

– The olfactory performance must be retained after storage at elevated temperature. This means that the encapsulated fragrance must stay inside the capsule during storage.
– The encapsulated olfactory palette must be as wide as possible to ensure clear superiority over the equivalent investment in free oil.
– The amount of formaldehyde in the delivered slurry as well as in finished products (softeners) after storage must be far below 50 ppm.

These objectives are conflicting:

– A microcapsule with a high amount of melamine formaldehyde resin can be highly stable with a hard and thick shell. However, it is assumed that its ability to release fragrance without rubbing will be very low and the amount of formaldehyde generated very high.
– In contrast, it is assumed that a microcapsule with a low amount of melamine formaldehyde resin will be more fragile and easily breakable. Moreover, the amount of formaldehyde generated will be very low. However, its ability to retain fragrance during storage will be reduced.

After a presentation of the melamine formaldehyde process and its key parameters, this article will describe the Mechacaps™ technology and its ability to answer these main challenges.

3. Aminoplast or MF Microcapsules

3.1 *Process*

The melamine formaldehyde process involves three steps (Fig. 2):

– In a first step, an emulsion is formed by mixing the perfume with the aqueous phase containing the monomers (melamine formaldehyde precondensate) and optionally a protective colloid in water. The droplet size is adjusted by varying the stirring speed.
– After activation of the polycondensation by a pH shift, the reaction mixture is kept for several hours at low temperature to enable the formation of pre-polymer which deposit on the O/W interface. The droplet size is adjusted by varying the stirring speed.
– The temperature is increased to crosslink the polymer shell.

3.2 *Melamine Formaldehyde Precondensate*

The reaction between melamine and formaldehyde was discovered by Liebig[16] in 1834 and its first industrial use was reported in 1936.

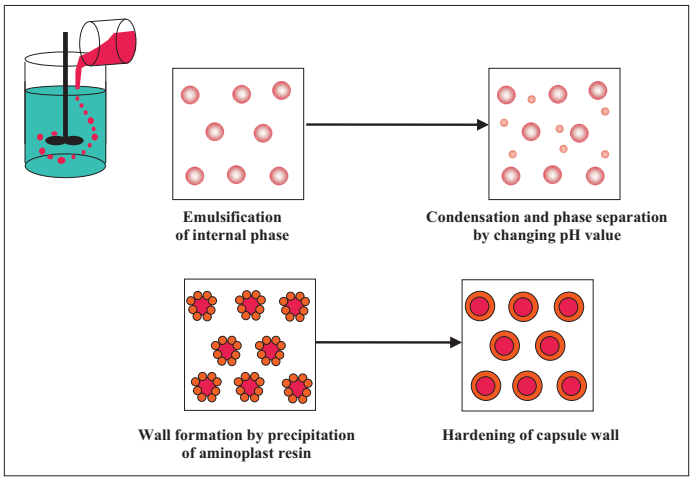

Fig. 2. Microcapsule synthesis scheme.

(1) R-NH_2 + **HCHO** ⇆ R-NH-**CH_2-OH** *H^+ catalyzed*

(2) R-NH-**CH_2-OH** + R-NH-CH_2-OH ⇆ R-NH-**CH_2-O-CH_2**-NH-R + H_2O *H^+ catalyzed*

(3) R-NH-**CH_2-OH** + R-NH_2 ⇆ R-NH-**CH_2**-NH-R + H_2O *H^+ catalyzed*

The condensation in the absence of water is essentially a thermally catalyzed and quite uncontrollable reaction. The conversion of melamine into methylolated melamine pre-condensate was used in the early forties as a way to better control the reaction. However, such pre-condensates were quite reactive and suffered from limited shelf life. Alkylation with short chain alcohols was finally used to stabilize the pre-condensate.

Highly methylolated melamine pre-condensates were patented by CIBA in 1942 and commercialized in 1950 in combination with polyester for wire coatings.

MF microencapsulation requires these highly methylolated melamine pre-condensates for two main reasons: i) the native melamine is not soluble in water, while the pre-condensate is and ii) the condensation in water relies on acid catalysis, which is better controllable than thermal catalysis. This is the essence of the NCR[17] and BASF[18] processes originally developed for pigment encapsulation and then transposed to liquid encapsulates, such as perfume.[19]

BASF patented a series of water soluble, highly methylolated and partially methylolated pre-condensate in water/methanol/formaldehyde solution under the name Luracoll®. The complete polycondensation of melamine with formaldehyde is summarized in Fig. 3.

Other suppliers like Cytec offer a wide range of MF resins precondensates, which boast very low formaldehyde release upon curing.

3.3 *Protective Colloid*

BASF recommends to use Luracoll in combination with a specific protective colloid (Lupasol type), described as a copolymer of acrylamidopropylsulfonate (AMPS) and methacrylic acid/acrylic acid (MA/AA).

Other kinds of protective copolymers based on acrylics or alcohols can be used in melamine formaldehyde microcapsules.[20] However, recent literature suggests that competitive adsorption at the interface with mixture of surfactants results in the formation of macroholes, and ultimately encapsulation failure.[21]

3.4 *Residual Formaldehyde Level*

The involvement of formaldehyde at various stages of the microencapsulation process is a widely recognized issue. This

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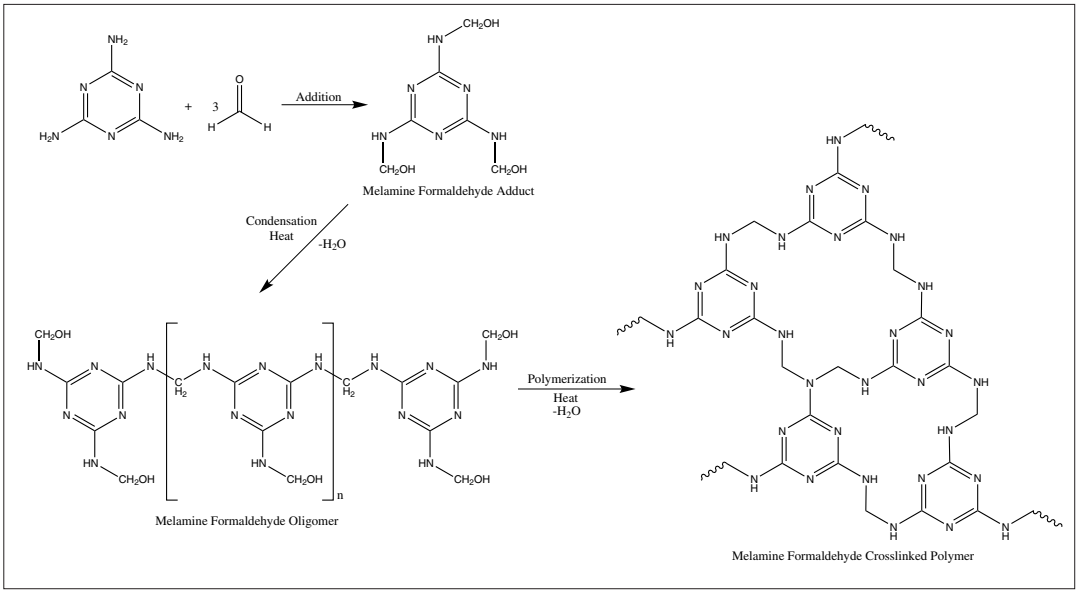

Fig. 3. Melamine formaldehyde polycondensation.

problem is more acute in microencapsulation than in coating, which is due to the fact that highly methylolated reagents are used in the former case. In the polycondensation process, formaldehyde (HCHO) enters either as free monomer or in nascent form, *i.e.* bound to the melamine moieties in the form of methylol groups, However, during polycondensation formaldehyde can be incorporated into the membrane when reaction (1) to (3) occurs or released from it when reaction (4) to (6) occur:

(4) Polycondensation step to methylene bonds
R-NH-CH_2OH + R-NH-CH_2OH ⇆ R-NH-CH_2-NH-R +H_2O + **HCHO**

(5) Degradation of methyleneoxy bond and formation of methylene bonds
R-NH-CH_2-O-CH_2-NH-R ⇆ R-NH-CH_2-NH-R + **HCHO**
H^+ catalyzed

(6) Demethylolation of the unreacted groups
R-NH-CH_2-OH ⇆ R-NH_2 + **HCHO**

where R designates a polymer, melamine, urea, benzoguanamine, and, more generally, any suitable polyamine residue.

As a main consequence of the reactions (4) through (6), formaldehyde is often generated during the polycondensation itself or during aging, especially in acidic media, leading to high levels of free formaldehyde in the end product. Furthermore, it will be obvious to the chemist that reaction (1) will especially occur if the aminoplast resin has a high level of unreacted methylol groups, *i.e.* in the case of incomplete cross-linking of the resin, while the extent of reaction (3) will depend on the methylene to methylenoxy group ratio achieved at the end of the process. Another consequence of reactions (1) through (3) is the occurrence in equilibrium of a significant level of free formaldehyde in systems containing microcapsules that are kept at low pH for a long period of time. This renders this system unsuitable for a liquid fabric softener with a pH typically in the range of 2 to 4.

BASF discloses an alternative way to reduce the residual formaldehyde level of aminoplast microcapsules[22] by post-adding a primary, secondary or tertiary amine, or ammonia, to an aminoplast microcapsule slurry obtained by polycondensation of melamine, formaldehyde, methylolated melamine, and a protective colloid in the presence of short chain linear alcohol and water. With this method, the residual formaldehyde level in the microcapsule slurry can be decreased by a factor 10 to *ca.* 0.36 wt% (3600 ppm), as measured according to DIN 16746. BASF also discloses a process to obtain melamine-formaldehyde microcapsule slurry with low viscosity and reduced formaldehyde content,[23] where melamine is added during the curing phase. An alkaline metal salt of a copolymer of 2-acrylamido-2-methylsulfonic acid is used as colloid stabilizing agent. Using this process, the formaldehyde level is further decreased by an order of magnitude to reach 80–400 ppm as measured according to DIN EN 645 and DIN EN 1541.

A number of procedures have been suggested which recommend the post-addition of so-called formaldehyde scavengers, such as ammonia, glycine, urea, melamine, ethylene urea, sodium bisulphite, acetoacetamide, cysteine hydrochloride and the like. However, using un-carefully selected scavengers may also displace the chemical equilibria discussed above and has, therefore, a limited action in time. On long-term storage, some scavengers can potentially interact with the microcapsule shell and then impact the microcapsule stability in bases.

4. Innovation through Givaudan Mechacaps™

To achieve optimal MF microcapsules properties, several processes have been developed by Givaudan. These microcapsules have been tested from a stability point of view in commercial bases such as fabric softeners. Their mechanical properties have been measured with a nano-indenter.[24]

The first formulations developed were acceptable from a mechanical point of view but were not stable in commercial bases. The main challenge Givaudan had to solve was to improve the stability without affecting the mechanical properties of microcapsules. This was addressed by an adjustment of the shell thickness and a proper choice of raw materials type and amounts. In the meantime, the amount of residual formaldehyde also had to be reduced.

Beyond process solutions, it has been necessary to adjust the microcapsules composition in order to optimize breakability, stability and performance. Fig. 4 shows that when microcapsules are too small (below 10 microns), microcapsules are not broken and performance on dry cloth is limited. If microcapsules are too big (above 30–40 microns), microcapsules are too fragile. Moreover, deposition on fabrics is not optimized. The best compromise is a microcapsule size between 10–40 microns.

4.1 *Shell Condensation*

It is known that addition of polyols, and especially aromatic polyols, combined with formaldehyde effectively decreases the

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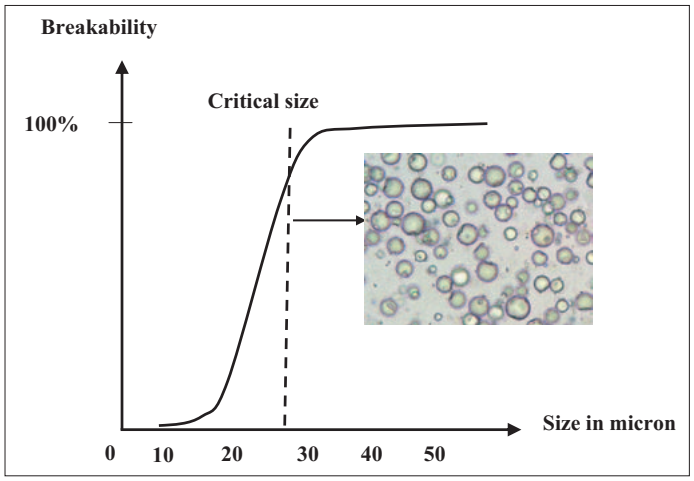

Fig. 4. Breakability of microcapsules vs microcapsule size.

permeability of gelatin coacervate microcapsules[25] under acidic conditions and moderate reaction temperature. The same procedure has been applied to gelatine, polyvinylalcohol[26] and cationic starch microcapsules. The possibility to apply this procedure to aminoplast resin has been proposed but not specifically exemplified. In all of the above developments using hydroxyl aromatic compounds, the hydroxyl aromatic compound is always used in combination with an aldehydic material, especially formaldehyde, or provided to the cross-linking reaction in the methylolated form, which resulted in a decrease of the nascent formaldehyde level in the product.

Incorporation of hydroxyl-bearing compounds as a co-monomer into the polymer shell led to significant improvement in perfume retention during storage.[27]

4.2 *Protective Colloid/Templating Agent*

There is also significant literature suggesting the use of anhydride copolymers for melamine-formaldehyde capsule preparation.[28] The literature also suggests that the anhydride acts to stabilize the emulsion and forms a reactive 'foothold' or catalyst for pre-polymer wall formation.[29] Speculation still exists regarding the exact reaction mechanisms involved between the anhydride copolymer and the MF prepolymer. However, anhydride copolymers are very reactive towards amidation, esterification and hydrolysis, forming amphiphilic, interfacially active polymers commonly used in coating, as dispersing agents, and emulsifiers. Their high reactivity, and their significant increase in polarity during the course of the amidation reaction, has been utilized in a number of *in situ* and interfacial encapsulation methods.

Givaudan found that the use of anhydride copolymers improves the stability of the capsules with respect to surfactant, thus improving perfume retention properties and enabling use of the capsules in aqueous surfactant containing products in a way that has not hitherto been possible.[31]

4.3 *Reducing the Formaldehyde Level*

A major drawback of the MF process is the presence of appreciable amounts of residual formaldehyde in the slurry after the microencapsulation has been completed. Usually, formaldehyde is neutralized in alkaline conditions by addition of ammonia. However, the residual is still too high and several parameters have been optimized to reduce this amount.

The residual HCHO levels in the slurry of the microcapsules were significantly decreased with the optimization of the raw material mixture and the optimization of process parameters as described above. To further decrease the amount of residual formaldehyde, in acidic media, scavengers such as ammonia, urea and its derivatives are used in Mechacaps™ technology.

Other kind of aldehydes can be used to replace formaldehyde. Recently, Givaudan developed a microcapsule comprising a core of fragrance and a shell of aminoplast polymer.

The capsules are competitive with known aminoplast capsules and have the major advantage that they are formaldehyde-free. They consist of:

– polyamine moieties derived from at least one of urea, melamine, 6-substitued 2,4-diamino-1,3,5- triazin and glycoluril;[3]
– polyol;
– substituted methylene moieties such as dimethoxyethanal melamine precondensate or methylglyoxylatemethylhemiacetal.

Combination of these types of aldehydes with methylolated melamine has also been a way to significantly reduce the level of free formaldehyde in the slurry.

In Givaudan microcapsules slurries, this amount is far below 50 ppm.

5. Consequences and Properties of the Mechacaps™ System

5.1 *Enlargement of the Olfactory Palette*

In flavors, cosmeto-textile, and phase-change material fields, microencapsulated hydrophobic compounds often have a molecular weight above 400 g/mol. In the fragrance industry, fresh compositions contain mixtures of fragrance raw materials which all exhibit a molecular weight below 400 g/mol and more specifically below 250 g/mol for 'fresh notes'.

The optimization of raw material mixtures and the increase of shell network density made the encapsulation of highly volatile perfumes possible, with molecules exhibiting molecular weight as low as 150 g/mol, which induced an enlargement of the palette of perfume oils available as microcapsules, encapsulated in the standard MF process.

Once the Mechacaps™ processes were developed, a study of the optimization of encapsulated fragrances has been carried out involving a strong collaborative work with perfumers.

Starting with a selection of 400 raw materials, 60 mixtures have been totally analyzed in an experimental design mode. Performance on dry cloth without rub was measured by headspace techniques. Even though most of the molecules exhibit a reduced diffusivity through the shell, we have discovered that some molecules are able to plasticize the shell and increase the overall diffusion pattern of the perfume composition. Despite the complexity of these systems, an experimental algorithm has been developed to extract the best perfumery rules.

Thanks to our understanding of perfumery rules, we are now able to supply a full system which combines free and encapsulated fragrances. These compositions are outside of any existing patented space.

5.2 *Performance*

The advantage of Mechacaps™ against classical perfumery or microcapsules is represented in Fig. 5. In the introduction, we saw that the olfactory performance is quickly lost during drying after the washing cycle in classical perfumery. When using a classical melamine formaldehyde capsule, a boost is obtained upon rubbing on in-wear. However, between the end of the washing cycle and the in-wear step, consumers do not experience an actual benefit. Thanks to its diffusivity, Givaudan Mechacaps™ performs on dry fabric without rub but also in-wear after rubbing. The whole freshness profile, from neat to long-lasting stage, is maximized and reaches consumer expectations when the Givaudan Mechacaps™ is associated with a tailor-made free perfume.

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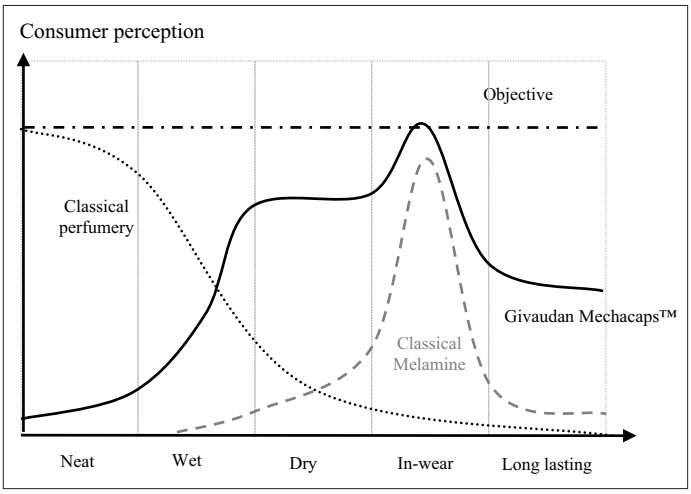

Fig. 5. Perfume release profile on a towel washed with non-encapsulated oil or encapsulated oil.

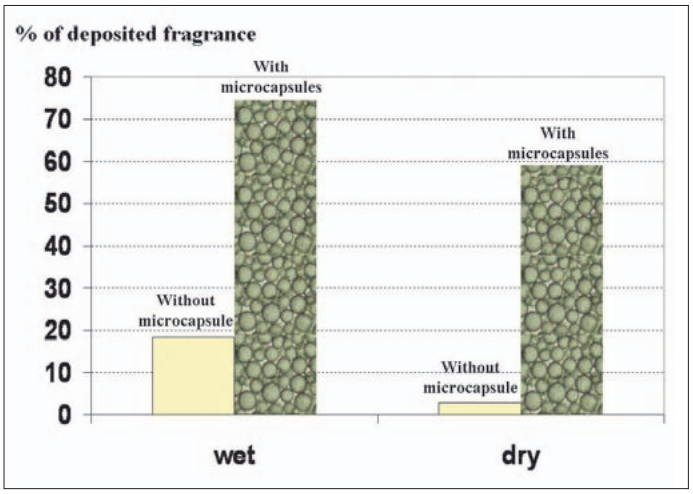

Fig. 6. Quantity of free oil versus encapsulated oil deposed on wet and dry fabrics (liquid fabric softener).

The performance profile of the finished product is still perceivable after storage.

Another advantage of Givaudan Mechacaps™ is its ability to deposit fragrance on fabrics. Microcapsules allow a deposition 10 to 20 times higher than the same non-encapsulated fragrance thus offering the advantage of optimizing the amount of fragrance to be used (Fig. 6).

6. Conclusion

Givaudan Mechacaps™ was specifically designed to answer these main challenges:

– Delivering an olfactory performance on dry fabric after several weeks of storage in softeners which is better than the one obtained with the free perfume. Not only do Givaudan Mechacaps™ give a clear olfactory 'boost' after gentle friction of the fabrics, but they also provide a continuous release of perfume on dry fabrics, thanks to their thoroughly controlled diffusive properties.
– The olfactory performance is retained after storage as most of the encapsulated fragrance stays inside the capsule during storage.
– The olfactory palette has been optimized to be as wide as possible. Thanks to our own understanding of perfumery rules, we are now able to supply a full system which combines free and encapsulated fragrances. These compositions are outside our competitor's patent spaces.
– The use of specific protective colloid compounds allows us to decrease the amount of polymer in the shell and the amount of formaldehyde. Moreover the use of scavenger such as ammonia and urea derivatives guarantees that the amount of released formaldehyde in finished products (softeners) after 1 month at 37 °C is below 10 ppm.

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[1] NCR, US patent number US2800458, **1957**.
[2] K. S. Lee, M. Rodson, H. B. Scher, *Pesticide Sci.* **1998**, *4*, 394.
[3] 'Encapsulation technologies for active food ingredients and food processing', Ed. N. J. Zuidam, V. Nedovic, Springer, **2010.**
[4] Outlast, US patent number US 6207738, **2001**.
[5] G. Nelson, *Int. J. Pharmaceutics* **2002**, *242*, 55.
[6] International Flavors & Fragrances, European Patent number EP 1719554, **2006**.
[7] M. Mccoy, *Chem. Eng. News* **2008**, *86*, 12.
[8] Ciba, GB patent number GB1156725 and US patent number US3594328, **1969**.
[9] Fuji, US Patent number US 3981821, **1974**.
[10] National Cash Register, US Patent number US 4100103, **1976**.
[11] BASF, US Patent number US 4406816, **1983**.
[12] BASF, US Patent number US 4898696, **1990**.
[13] P&G, US Patent number US 5066419, **1991**.
[14] IFF, US Patent number US 20050112152, **2005**.
[15] IFF, European Patent number EP 1797946, **2007**.
[16] J. Liebig, *Annalen der Chemie* **1834**, 10.
[17] NCR, US Patent number US 4100103, **1978**.
[18] BASF, US Patent number US 4406816, **1983**.
[19] BASF, US Patent number US 4898696, **1990**.
[20] H. Yoshizawa, E. Kamio, N. Hirabayashi, J. Jacobson, Y. Kitamura, *J. Microencapsulation* **2004**, *21*, 241.
[21] E. Kamio, S. Yonemura, T. Ono, H. Yoshizawa, *Langmuir* **2008**, *24*, 13287.
[22] BASF, US Patent number US 6261483, **2001**.
[23] BASF, US Patent number US2003/0004226, **2003**.
[24] H. Wang, P. Shi, H. Yu, W. Zhang, B. Xu, *Key Eng. Mater.* **2008**, *373*, 802.
[25] Fuji, US Patent number US 3965033, **1976**.
[26] NCR, US Patent number US 3755190, **1973**.
[27] Givaudan, WO Patent number WO200809838, **2008**.
[28] H. Yosjizawa, E. Kamio, E. Kombayashi, J. Jacobson, Y. Kitamura, *J. Microencapsulation* **2007**, *24*, 349.
[29] A. Shulkin, H. D. H. Stover, *J. Membrane Sci.* **2002**, *209*, 421.
[30] Quest International, US Patent number US 7238655, **2007**.
[31] Givaudan, WO Patent number WO 2009/100553, **2009**.