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Preparation and application of rose oil capsules onto printable paper

ABSTRACT

In this study, rose oil was encapsulated with stearic acid substituted polyvinyl alcohol macromolecule. In the first part of the study, stearic acid substituted polyvinyl alcohol macromolecule was synthesized and its chemical structure was elucidated by ATR-FTIR and ^{1}HNMR. Then, rose oil was encapsulated using this obtained polymer. The chemical structure of the obtained capsules was made by ATR-FTIR, and dimensional analysis was done by scanning electron microscope (SEM). After the obtained capsules, a paper coating formula was prepared and coated on 80 g/m² paper. The resulting scented papers were printed using the screen printing technique. The color, gloss, and deformation of the capsules on the surface of the printed and unprinted papers were determined by spectrophotometer, glossmeter and SEM. As a result, it was determined that the synthesized polymer could encapsulate the rose oil and the papers using these capsules could be printed without deformation.

KEY WORDS
Printability, encapsulation, rose oil, coating

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Introduction

Products with added value affect the purchasing behavior of customers. Papers with scented properties are one of them. Fragrance comes with perfumes, essences, or scented oils. While fragrant oils have advantages such as being natural and being more intense, they have disadvantages such as their prices and low production efficiency. All odors lose their effect after a while in contact with the air. In this sense, odors must be preserved. One of the methods to be used in the storage of fragrances is encapsulation. In the encapsulation, the liquid, solid or gaseous odorous content is covered with a polymeric wall and is pressure-sensitive released at the desired time. In this way, both odor is preserved, and it can be distributed more easily in ink or coatings.Fragrances are materials that are frequently used in our daily lives to attract attention and increase appetite. Fragrances are quickly affected by external effects such as oxygen and light (Barret, Beaulieu & Shewfelt, 2010). For this reason, they decompose rapidly, and odors exposed to open air spread rapidly and move away from the material to be odorized, and the desired property is quickly lost. For this reason, the odor must be preserved until it reaches the end user. With the developing technology, microcapsules can be used effectively in the protection, storage and distribution of chemicals that are rapidly affected by the external environment, degrade quickly, and have problems of dispersion in the materials to be used (I Ré, 1998). Scented papers are used in many areas such as packaging papers, tissue papers, personalized products, or catalogs. Fragrances can be imparted to the paper by surface coating during or after the production of the paper. The biggest problem with scented materials that will be added to the paper content is the dispersion problem of the scented materials in the paper or coating formulation and the rapid loss of the scent. For this reason, microencapsulation can be made to produce scented paper, and the scent can be stored for a longer time and released at the desired time (Ichiura, Sakamoto & Ohtani, 2016). Many odorants can be obtained from natural sources. The obtained natural origin scenting materials can be essences or essential oils (Sharmeen et al., 2021). Due to the developing technology and the

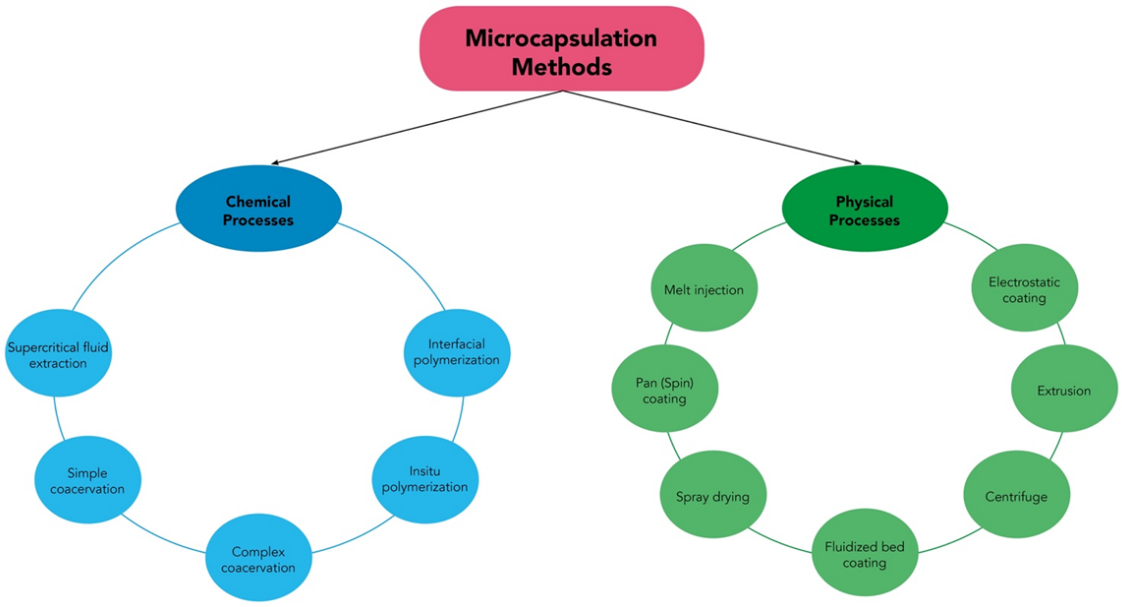
demand for healthy nutrition, return to nature and sustainability, the use of essential oils as fragrance materials is increasing day by day. Examples of essential oils used as fragrances are lavender oil, rose oil, peppermint oil, lily oil, rosemary oil, and geranium oil. Naturally sourced fragrant essential oils degrade rapidly, and it is seen as an effective method to produce microcapsules with natural shells to last until the end product use (Martins et al., 2014). The release mechanisms of encapsulated materials depend on the purpose of encapsulation. The encapsulated material can be released by external pressure, abrasion, heat, and diffusion (Milošević et al., 2017). For example, odors used in textile applications can be released by abrasion of the microcapsule wall in washing machines and dryers (Jyothi et al., 2012). Or scents applied on paper can be released by the effect of pressure. The encapsulation process provides a controlled release of fragrance compounds at the desired time. Relatively volatile components can be converted into stable components that inhibit rapid evaporation. In addition, the encapsulation technology provides environmental protection by reducing the waste of components. At the same time, material utilization and storage stability are improved by encapsulation (Ding et al., 2020). Timely and targeted release improves cost-effectiveness for manufacturers, thus improving desirability and marketing concept. Microcapsule production techniques are examined in two main groups as chemical and physical methods (Figure 1) (Jamekhorshid, Sadrameli & Farid, 2014).

In choosing the encapsulation method, the chemistry and properties of the inner and shell material, the diameter of the capsule, the permeability of the shell material, and the place and purpose of use of the capsule are taken into consideration (Augustin & Hemar, 2009).

Microcapsules have been frequently encountered in all areas of life for many years. The most used areas of microencapsulation applications are cosmetics, cosmetics textiles, paper and non-woven materials, graphic arts and printing industry, textile industry, special coatings and deodorants, food industry, detergent-phytosanitary products, biotechnology, electronics, medicine, pharmacy, agriculture, construction, waste treatment, chemical industry, photography etc. (Dubey, 2009).

With the addition of odor perception thanks to microcapsules to visual and tactile quality in printing technologies, we achieve more in terms of quality (Urbas et al., 2017). The value of products can be increased with prints where memories are recreated, emotions are enhanced, or scents with calming properties are applied. Microcapsules are often used in “scratch-n-smell” applications, such as perfumes in newspaper and magazine supplements, and stickers in “peel-a-part” applications, such as promotional advertising campaigns, children’s books, and cookbooks (Cleary et al., 2010). The main advantage of applying microcapsules with a specific printing technique is that the microcapsules can be applied to the target areas of the substrate and homogeneously (Starešinić, Šumiga & Boh Podgornik, 2011).

Fragrant essential oils that can evaporate at room temperature are materials produced from different parts of fruits and annual and perennial plants with strong aromatic odor properties. Due to their structure, they are available in very light yellow colors, which can evaporate in the liquid phase under standard conditions and can easily form solid crystals (Lee, 2003). These materials, which are also called essences due to their attractive odor, show etheric properties (Spence, 2021). These



» **Figure 1:** *Microcapsule production techniques*

oils, which have a long chain organic structure, undergo phase separation with water (Dhifi et al., 2016). Oils are used in the preservation of food and beverages with their properties such as slowing and preventing decay, slowing oxidation, accelerating destruction, and accelerating the reaction with enzymes. Essential plant-based oils are generally defined by the U.S. Food and Drug Administration (FDA) as GRAS, or generally safe (Prakash et al., 2015). Essential oils are aromatic compounds widely used in the perfume, pharmaceutical, and food industries. Essential oils are a mixture of more than 200 different compounds. These compounds consist mainly of monoterpene and sesquiterpene hydrocarbons and their oxygenated derivatives such as esters, alcohols, aldehydes, and ketones (Arman Kandirmaz et al, 2020). The ingredients obtained from the rose are used in cell renewal, correction of deformation and in the treatment of some diseases. It is also known that rose extracts are used in the treatment of stress and anxiety disorders (Happy, Jahan & Momen, 2021). When the extracts obtained from the rose were examined, it was determined that the source of the odor was monoterpene alcohols linalool, citronellol, ethers and linear carbon compounds with high molecular weight, esters, and phenols. Apart from these, β-damacenone, β-damacene, β-ionene are among the components that contribute to the odor in trace amounts (Erbas & Baydar, 2016).

In this study, the encapsulation of fragrant oil produced from roses grown in Turkey with stearic acid substitute polyvinyl alcohol (PVA) shell material, the coating of the produced capsules on paper and the printability of the coated papers were investigated.

Materials and methods

Materials

Polyvinyl alcohol, stearic acid, sulphuric acid, and ethanol were obtained from Sigma-Aldrich Chemie GmbH, Switzerland. Rose oil was purchased from a local market. White color base paper was used in the study. The technical specifications of the base paper used in the study are given in Table 1.

Table 1
Technical properties of base paper used in the study

Properties	Standard	Base paper
Grammage (g/m²)	ISO 536	80
Thickness (µm)	TAPPI T411	177
Whiteness (D65/10) (%)	ASTM E313	97
Gloss (75°)	Tappi T480 OM-20	5.5

Methods

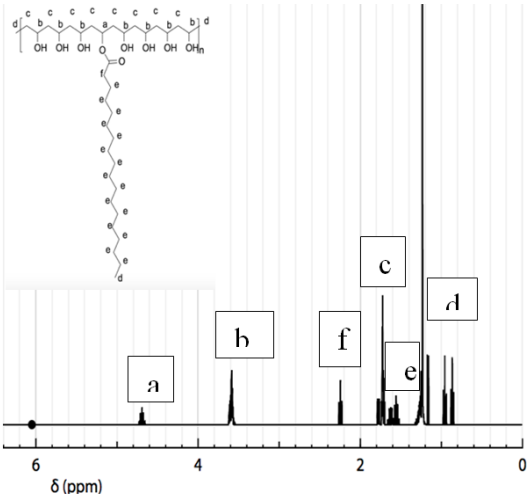
Stearic acid substituted polyvinyl alcohol polymer was synthesized by the acidic esterification method. For this purpose, PVA (40 mmol), 200 mL distilled water and stearic acid (10 mmol) were charged into a three-necked flask with nitrogen inlet, magnetic stirrer, thermometer, and reflux connected. While stirring in the oil bath at 250 rpm at 80 °C, 1 ml of H_2SO_4 was added dropwise with the help of a dropping funnel. The mixture was refluxed at 80 °C for 24 hours. The solution was precipitated with ethanol. The polymer was filtered and dried at room temperature in a vacuum oven overnight. The chemical structure of the produced polymer was elucidated by ^{1}HNMR and ATR-FTIR.

Encapsulation studies were carried out for rose oil with the polymer whose synthesis was described above. In the encapsulation study, 1 g of stearic acid substituted polyvinyl alcohol macromolecule was dispersed in 50 mL of distilled water, then 4 mL of 1M citric acid was added to the medium. 1 ml of rose oil was slowly added to the reaction vessel and mixed in a magnetic stirrer at 500 rpm for two hours to ensure encapsulation and complete interaction. The precipitate formed was removed from the liquid part, washed several times with distilled water to get rid of the chemicals trapped on the surface and dried in a vacuum oven. The morphological features of the produced capsules were elucidated by scanning electron microscopy (SEM) with Philips XL30 ESEM-FEG/EDAX. The microcapsules and coatings were brought to solid phase with liquid nitrogen, broken and then coated with platinum to prepare for SEM. Coating formulations with synthesized microcapsules were prepared in accordance with the literature. 7.5 grams of cationic starch was dispersed in 92.5 mL of water and stirred at 95 °C until the mixture became transparent. After it became transparent, it was stirred for another 10 minutes to be homogeneous at this temperature, then cooled to room temperature and added into 1 g of the produced microcapsules. The papers used in the coating were conditioned at 25 °C for two days. The coating formulations produced (with and without capsules) were coated on one side of the paper at 0.1 g/m² at room temperature with laboratory type K303 Multicoater (RK Print Coat Instruments Ltd, UK) using Mayer Rod 2 and dried freely. The coating machine speed was selected at 2 m/min and the average coating thickness of the paper coatings was set to 3 µm. Coatings containing cationic starch with and without capsule were examined with an X-Rite eXact handheld spectrophotometer to investigate whether the capsule changed color. The color difference of the coatings is calculated according to the ΔE2000 formula. The surface properties of the obtained coatings were investigated by scanning electron microscope (SEM). Gloss measurements were made with BYK-Gardner GmbH glossmeter with 60° geometry according to ISO 2813:2014.

In order to determine whether the capsules burst during printing and to determine the printability parameters, screen printing was carried out with magenta color screen printing ink with Arus semi-automatic screen printing machine with a 75° squeegee angle, 77 tpc weaving density, 75 shore hardness with doctor characteristics. The gloss measurements were made using the TAPPI T480 om-15 standard using the BYK Gardner gloss device on the prints. Color measurements were determined using an X-Rite eXact spectrophotometer according to the CIE Lab method.

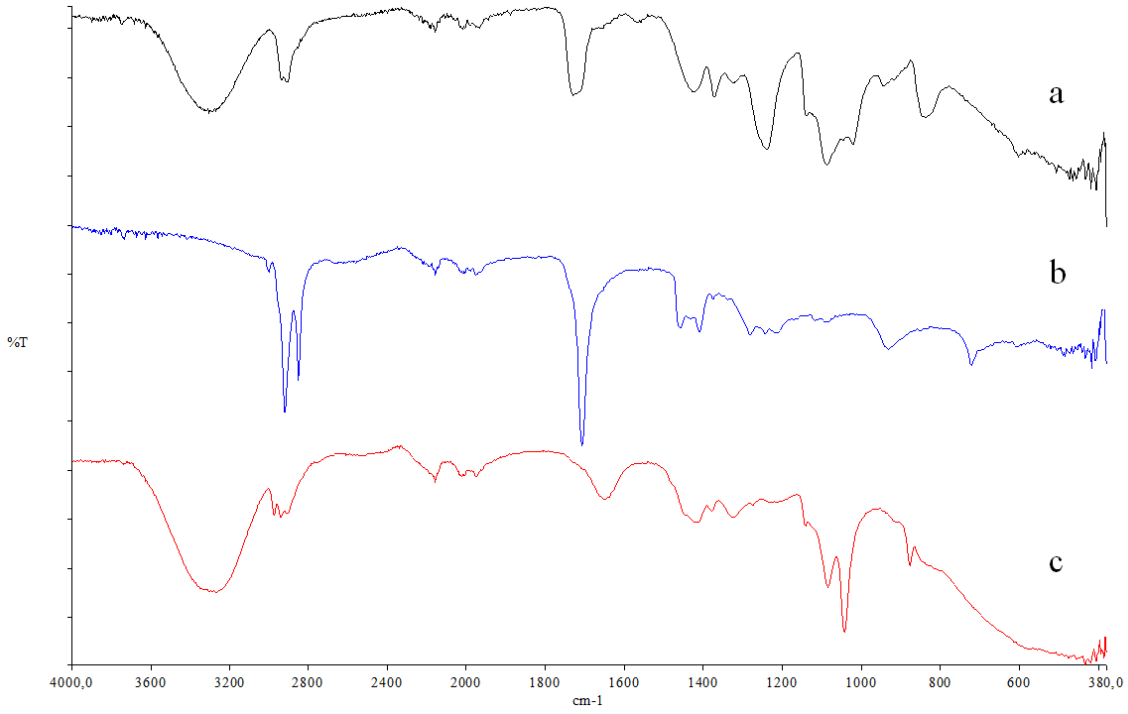
Results

The chemical structure of the synthesized Stearic acid substituted PVA polymer was elucidated by ATR-FTIR (Figure 2) and ^{1}H-NMR (Figure 3). ATR-FTIR and ^{1}H-NMR spectra confirmed the designed structure. When Figure 2.a is examined, characteristic C-H_2 asymmetric alkyl tensile bond vibration is observed for PVA at 2915 cm^{-1}. Also, the vibration of 3307 cm^{-1}-OH and crystalline PVA is 1090 cm^{-1}. In Figure 2.b, 3299 cm^{-1} hydroxyl vibration and 1711 cm^{-1} free carbonyl groups were exposed. Stearic acid substituted polyvinyl alcohol polymer ATR-FTIR spectrum is given in 2.c. The ester vibration clearly visible at 1644 cm^{-1} proves that the reaction has taken place and that the self-protection of the other peaks of stearic acid and PVA does not decompose. Figure 3 shows the characteristic ^{1}H-NMR signals of stearic acid substituted polyvinyl alcohol. The proton on the carbon to which stearic acid is attached was released at 4.69 ppm. In addition, the spectrum shows the proton of the hydroxyl bonded carbon at 3.59 ppm, protons symmetrical to PVA at 1.72 ppm, symmetrical protons on stearic acid at 1.23 ppm, symmetrical protons at the first carbon of stearic acid at 2.25 ppm and at 1.67-0.84 ppm the final protons are clearly visible. The ^{1}H-NMR spectrum proves that the synthesis was carried out successfully. In addition, the ratio of stearic acid PVA was calculated as 11%.



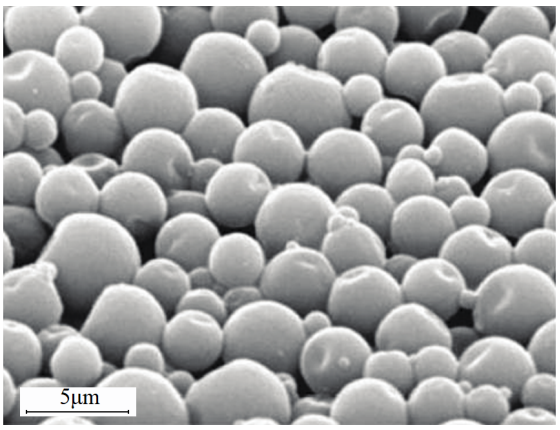
» **Figure 3:** *^{1}H-NMR spectrum of stearic acid substituted polyvinyl alcohol polymer*

Rose oil encapsulation with stearic acid substituted polyvinyl alcohol polymer was successfully performed. The morphological features of the obtained



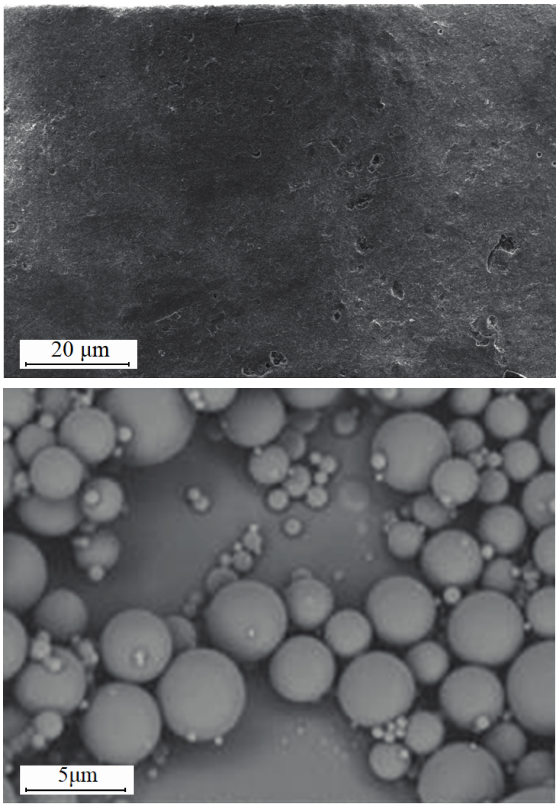
» **Figure 2:** *a) PVA, b) Stearic acid and c) Stearic acid substituted polyvinyl alcohol polymer ATR-FTIR spectrum*

capsules were elucidated by SEM (Figure 4). When the obtained SEM image was examined, it was concluded that monodisperse, homogeneously dispersed, 3 µm in size, and not fully spherical capsules with intermittent collapses were obtained.



» **Figure 4:** *SEM image of stearic acid substituted polyvinyl alcohol shell microcapsules with rose oil core material*

Coating formulations with or without synthesized microcapsules were prepared and coated on office papers. The surface properties of the obtained coatings were examined by scanning electron microscopy (SEM) (Figure 5).



» **Figure 5:** *SEM image of stearic acid substituted polyvinyl alcohol shell microcapsules with rose oil core material coated paper*

Stearic acid substituted PVA-rose oil microcapsules were agglomerated in the coating due to Van der Walls interactions between each other and cationic starch, and the distribution was determined to be heterogeneous. However, the capsules could be applied to the surface without any deformation.

The color and gloss properties of the coatings were examined and given in Table 2. When Table 2 was examined, it was determined that microcapsule coated papers were more yellow than normal papers with the change in b values. Also, when the reference value is uncoated paper, the color difference is below ΔE_{00} 3. It's a small change that can't be seen with the naked eye. and in the acceptable color range according to ISO12647. The yellowing in the color of coatings containing microcapsules is due to the color of the oils, which are the internal materials, as well as the chromophore groups in the structure of the polymers. When the gloss values were examined, it was found that it was more glossy than the uncoated paper but less glossy than the cationic starch coated paper. The capsules created a roughness on the surface, which reduced the gloss (Ozcan & Tutak, 2020).

Table 2

Color and gloss properties of uncoated, cationic starch coated, and stearic acid substituted PVA-rose oil capsule coated papers

Properties	Uncoated paper	Cationic starch coated paper	Stearic acid substituted PVA-rose oil capsule coated papers
L	90.87	89.65	90.46
a	2.29	2.19	2.63
b	-8.02	-5.6	-5.07
ΔE_{00}		2.03	2.48
Gloss (TAPPI 60°)	4.5	8.9	8.5

Screen printing was performed on uncoated papers, cationic starch coated paper and microcapsule (with steric acid substituted PVA shell and rose oil core) added coated papers with magenta color screen printing ink. The color and gloss of the obtained prints were measured and given in Table 3.

Table 3

Color and gloss properties of uncoated, cationic starch coated, and stearic acid substituted PVA-rose oil capsule coated papers

Properties	Printed Uncoated paper	Printed cationic starch coated paper	Printed Stearic acid substituted PVA-rose oil capsule coated papers
L	47.68	48.49	47.96
a	74.20	74.53	74.81
b	-3.48	-5.28	-3.97
Gloss (TAPPI 60°)	6.9	16.1	15.2

When the printing results were examined, the biggest change in color of coatings containing cationic starch occurred in the b value. This change in b value shifted the color slightly towards blue. On the other hand, in the capsule coated paper, this blue shift is reduced with the yellowish color of the oil and the capsule, and it is approached to the uncoated paper. When the color differences were examined, it was determined that the ΔE_{00} values of cationic starch coated paper and capsule coated paper were 2 and 0.86, respectively. These values are very small, and the color difference is too indistinct to be perceived by the naked eye. When the gloss results were examined, it was determined that the gloss of the print made on uncoated paper was lower by 2.5 times with the surface treatments. When the gloss results were examined, it was determined that the gloss of the print made on uncoated paper was 2.5 times lower than the surface treated (coated) papers. The results obtained are in line with the unprinted gloss.

Conclusions

In this study, stearic acid substituted polyvinyl alcohol macromolecule was synthesized. When the ATR-FTIR and ^{1}HNMR results were examined, it was determined that the synthesis was successful. Rose oil was successfully encapsulated in weak acidic medium using the related polymer and it was determined that the obtained capsules were monodisperse and 3 micrometers in size. Cationic starch binder paper coating formulations using the obtained capsules were prepared and applied to the paper surface without deformation. It was determined that the colors of the obtained coated papers were very close to the uncoated paper, and the deviation from the color was observed in the b axis due to the yellow color of the oil in general. Screen prints were made on uncoated and coated papers and color and gloss parameters were determined. It was concluded that the color difference decreased to 0.86 in printed capsule-coated papers and the color was so close to each other that it could not be perceived with the eye. As a result, it has been obtained that rose capsules are suitable to produce scented paper.

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