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# Direct Preparation of Gelatin Microcapsules on Paper Surface Using Simple Coacervation Technique

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**ABSTRACT:** A simple coacervation technique was used to coat a functional paper with gelatin microcapsules containing geraniol to prepare functional papers with sustained fragrance release. This method eliminated the need for microcapsule preparation and coating with a binder. A gelatin solution containing geraniol and Tween 20 was coacervated using sodium carbonate ($Na_2CO_3$) solution; the final $Na_2CO_3$ concentration in the solution was 5 wt %. Filter papers impregnated with the coacervation mixture were immersed in 0–20 wt % $Na_2CO_3$ solutions. Gelatin microcapsules were formed on the paper surface when 15 or 20 wt % $Na_2CO_3$ solutions were used. The maximum amount of geraniol was fixed on paper prepared under these conditions, and the percentage of residual geraniol in the paper (RES) was about 70% after 72 h; this value was much higher than that for a blank sheet. The formation of gelatin microcapsules was important for the fixation and sustained release of geraniol. © 2013 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 129: 2139–2144, 2013

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## INTRODUCTION

Microcapsules are useful for long-term protection of functional materials from environmental factors, for controlling the release of desired materials, and for the conversion of liquids to the solid state.[1–5] Microencapsulation of volatile essential oils (VEOs) such as aromatic materials is achieved by converting the liquid oil to a solid,[6–8] and enables sustained release of VEOs.

We have studied functional papers, which make use of the native properties of the materials they are made with, and can include adsorbents, antimicrobial agents, and conductive materials.[9–17] Functional papers that release fragrances are useful in applications such as insecticidal sheets that release an insect-repellant VEO.[17–21] For successful application, the paper needs to provide sustained release of the fragrance. In past studies, functional papers have usually been prepared from microcapsules with a binder.[8,22] In our previous paper, a functional paper was prepared using a geraniol-$Ca(OH)_2$ composite powder and a binder.[23] The preparation of sustained-fragrance-release functional papers using microcapsules and the geraniol-$Ca(OH)_2$ composite required two main steps. First, microcapsules containing the VEO or the powdered VEO were prepared, and then they were coated and fixed to the paper with a binder. A technique is therefore needed for fixing VEO-containing microcapsules or VEO powders to the paper surface without microencapsulation or powderization of the VEO and coating with a binder.[17,23–26] In this study, the direct preparation of gelatin microcapsules on the paper surface was achieved using coacervation. This technique can be used to prepare functional papers with sustained-release properties without microencapsulation and binder-coating processes, in one step.

Gelatin is used in food, pharmaceuticals, and photography.[27,28] Gelatin has also been widely used in the preparation of microcapsules, using a simple coacervation technique[29,30]; this is a physicochemical process based on polymer desolvation to form microcapsule walls. In a coacervation process, any hydrophilic soluble polymer can be used as a wall-forming material and coacervates in response to a phase-separation-inducing variable such as salt addition, pH, temperature, solvent concentration, or electrolyte concentration.[29,30] In our coacervation system, gelatin and sodium carbonate ($Na_2CO_3$) were used as the hydrophilic polymer and salt, respectively. We attempted to form gelatin microcapsules containing *trans*-3,7-dimethyl-2,6-octadien-1-ol (geraniol), a VEO, directly on the paper surface. If the geraniol is not microencapsulated, its fragrance disappears in a short time because of its high volatility. Paper with microcapsules containing geraniol can release the fragrance over a long time period.

When paper impregnated with a mixed solution of gelatin coacervated using $Na_2CO_3$ and geraniol is immersed in $Na_2CO_3$ solution, gelatin microcapsules are expected to form directly on

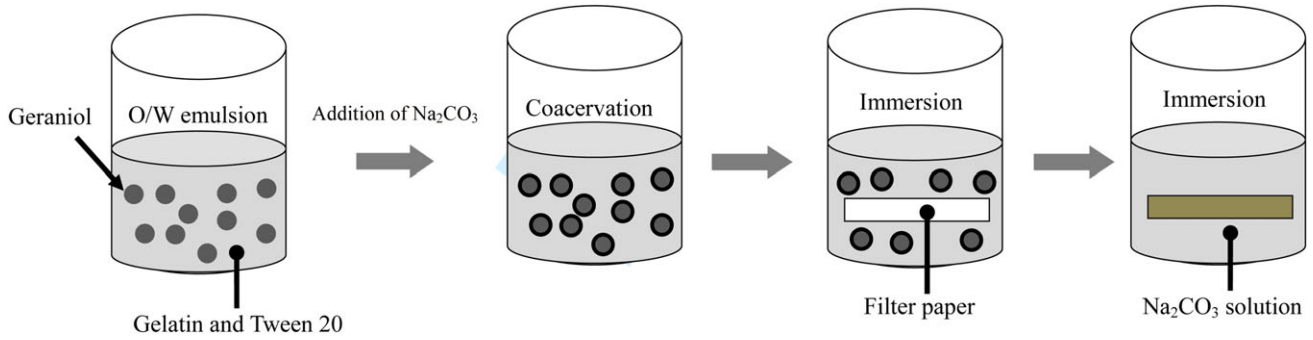


**Figure 1.** Preparation on paper surface of gelatin microcapsules containing geraniol. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

the paper surface. A technique that directly fixes gelatin microcapsules on paper surfaces without using a binder is useful for one-step preparation of paper-fixed microcapsules containing VEOs and imparting controlled-release functions to the paper.

The properties of geraniol-containing gelatin microcapsules on a paper surface, prepared using a simple coacervation technique, are presented in this report. The optimal conditions for preparation of the gelatin microcapsules on the paper surface were determined. Investigations were conducted on the effects of the $Na_2CO_3$ solution concentration on the formation of gelatin microcapsules, the retention of geraniol on the paper, and the controlled release of geraniol from the prepared paper.

## EXPERIMENTAL

### Materials

Gelatin (from bovine bone), geraniol (assay 90 wt %), polyoxyethylene sorbitan monolaurate (Tween 20), and anhydrous $Na_2CO_3$ were purchased from Wako Pure Chemical Industries Ltd., Osaka, Japan. Filter paper (No. 2, Advantec Co., Ltd., Tokyo, Japan) was used as the substrate. Acetonitrile and distilled water for high-performance liquid chromatography (HPLC) were purchased from Kanto Chemical Co., Inc., Tokyo, Japan.

### Preparation on Paper Surface of Gelatin Microcapsules Containing Geraniol

Figure 1 shows the method used to produce gelatin microcapsules on the paper surface. Geraniol (2.75 mL) was emulsified in an aqueous solution of 10 wt % gelatin (25 mL) containing Tween 20 (0.1 g). This mixture was kept at 40°C for 10 min under constant stirring (350 rpm), using a 35-mm magnetic stirrer, to yield an oil/water (O/W) emulsion. To start the coacervation, 20 wt % $Na_2CO_3$ solution (10 mL) was added to the O/W emulsion, and the system was kept at 40°C for 15 min under constant stirring (350 rpm). The resultant $Na_2CO_3$ concentration in the final coacervation mixture was 5 wt %. Filter papers (20 mm × 30 mm) impregnated with this coacervation mixture were immersed in 0–20 wt % $Na_2CO_3$ solutions for 10 min, and then air-dried for 24 h.

A blank paper was prepared using the following procedure and conditions. Geraniol (2.75 mL) was emulsified in an aqueous solution of distilled water (25 mL) containing Tween 20 (0.1 g) and 20 wt % $Na_2CO_3$ solution (10 mL) at 40°C for 10 min under constant stirring (350 rpm), using a 35-mm magnetic stirrer. A filter paper (20 mm × 30 mm) was impregnated with this geraniol-containing mixture and then air-dried for 24 h.

The reference paper was prepared as described in our previous paper.[23] A mixture of CaO (8 g) and geraniol (4 g) was agitated, using a magnetic stirrer, for 5 min at 15°C. During this time, distilled water (10 mL) was added dropwise to the mixture. The geraniol-$Ca(OH)_2$ composite was dried at room temperature and then stored in a refrigerator at 4°C. The geraniol-$Ca(OH)_2$ composite (50 mg) was uniformly fixed on a 30 mm × 20 mm paper. This paper was immersed in 0.1–1.0 wt % sodium alginate solution (50 mL) for 5 min, and then dried at room temperature for 24 h.

### Characterization of Paper Fixed With Gelatin Microcapsules Containing Geraniol

Fourier transform infrared (FTIR) attenuated total reflection spectra were obtained using an FTIR-61000 (JASCO Inc., Easton, MD) spectrometer at a resolution of 4 $cm^{-1}$. Forty scans were accumulated in the spectral range 4000–550 $cm^{-1}$. The paper surface was analyzed using scanning electron microscopy (SEM; VE-9800, Keyence Corp., Osaka, Japan) with an accelerating voltage of 5.0 kV, after osmium-coating (Neoc-ST, Meiwafosis Co., Ltd., Tokyo, Japan).

The tensile strength of the paper prepared by coacervation was determined using a tensile tester (STB, A&D Co., Ltd., Tokyo, Japan). The specimen size was 25 mm × 30 mm. The test speed and span distance were 10 mm/min and 5.0 mm, respectively.

### Evaluation of Geraniol Fixation in Gelatin Microcapsules Prepared on Paper

The geraniol in the prepared paper was extracted using ethanol (4 mL) and ultrasonication for 5 min. After filtration of the solution, using a membrane filter, a 1-$\mu$L aliquot was subjected to HPLC analysis without further purification. The geraniol concentration was determined using an HPLC (2695 Separation Module, Waters, Milford, MA) equipped with a C18 column (Inertsil ODS-3, GL Sciences Inc., Torrance, CA, 150 mm × 4.6 mm) and a UV detector (210 nm). The mobile phase was 70% (vol/vol) acetonitrile/30% (vol/vol) distilled water, with a constant flow rate of 1.0 mL/min. The column temperature was 40°C.

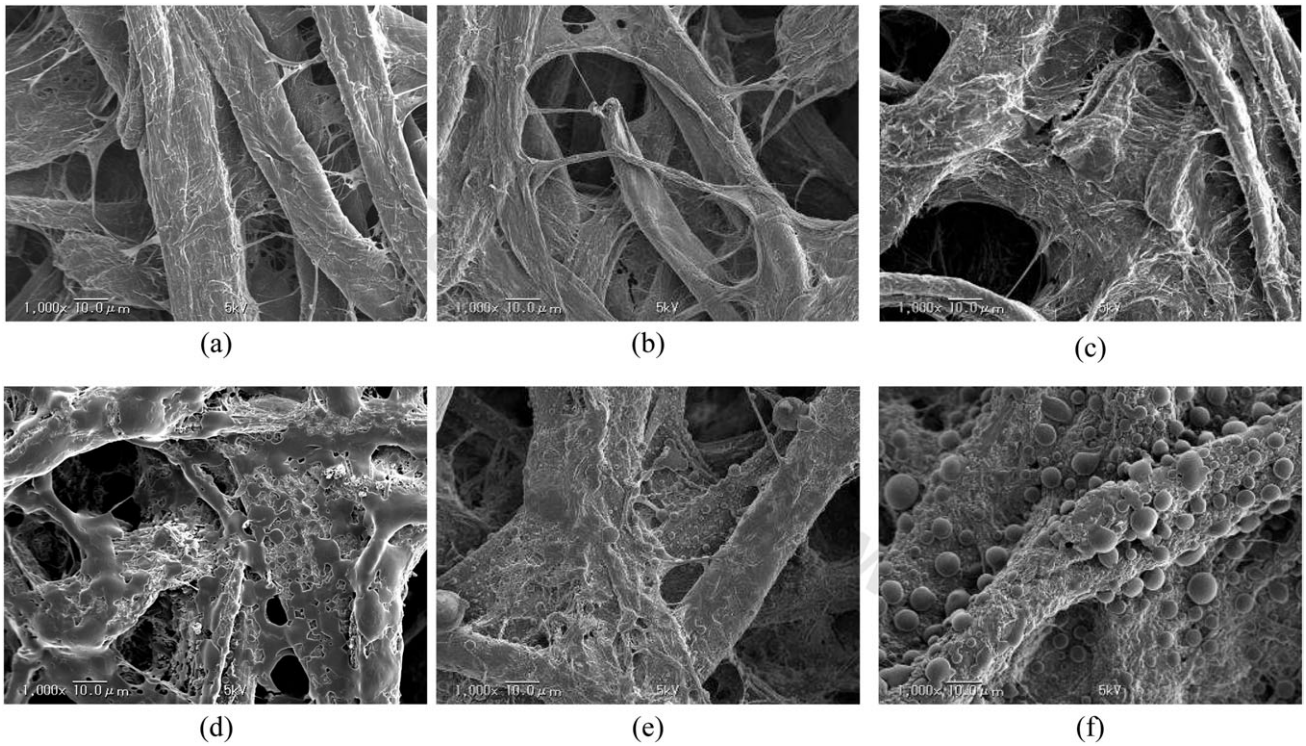


**Figure 2.** SEM images of (a) filter paper before coacervation treatment, and of papers prepared using (b) 0 wt %, (c) 5 wt %, (d) 10 wt %, (e) 15 wt %, and (f) 20 wt % $Na_2CO_3$ solutions.

### Evaluation of Geraniol Release From Paper

The prepared paper was placed in a 50-mL vial at 25°C for 0–72 h. Any residual geraniol was extracted from the paper using 4 mL of ethanol and ultrasonication for 5 min. The concentration of geraniol in the extract was analyzed using HPLC under the same experimental conditions as described above. The percentage of residual geraniol in the paper (RES) was evaluated from RES (%) = $(RES_1/R_0) \times 100$, where $RES_1$ (g/m$^2$) is the amount of residual geraniol in the paper after 24 h, 48 h, or 72 h, and $R_0$ (g/m$^2$) is the amount of geraniol fixed on the paper.

The geraniol release functions of the reference paper prepared using the geraniol-$Ca(OH)_2$ composite powder and a binder, and of the papers prepared by coacervation, were compared.

## RESULTS AND DISCUSSION

### Effect on Gelatin Microcapsule Formation of $Na_2CO_3$ Concentration

**Morphology of Gelatin Formed on Paper Surface Using Simple Coacervation Technique.** Figure 2 shows the SEM images of papers prepared using 0–20 wt % $Na_2CO_3$ solutions for impregnation of filter papers immersed in a coacervation mixture of gelatin–$Na_2CO_3$ containing geraniol. In the case of 0 wt % and 5 wt % $Na_2CO_3$ solutions, the formation of gelatin microcapsules was not observed [Figure 2(b,c)]. When the paper was prepared using 10 wt % $Na_2CO_3$, film formation was observed [Figure 2(d)]. As shown in Figure 2(e,f), microcapsules were formed on the paper surface with 15 wt % and 20 wt % $Na_2CO_3$.

**Characterization by FTIR of Gelatin Formed on Paper Surface Using Simple Coacervation Technique.** Figure 3 shows the FTIR spectra of paper surfaces treated under various conditions. The peaks at 1200–900 cm$^{-1}$ were attributed to cellulose peaks (C—O and C—O—C stretching vibrations) [Figure 3(a)]. Peaks attributed to geraniol were observed at 1664 cm$^{-1}$ (C=C stretching vibrations), 1436 cm$^{-1}$ and 1374 cm$^{-1}$ (C—H bending vibrations), and 991 cm$^{-1}$ (C—O stretching vibration) [Figure 3(g)]. Gelatin is composed of polypeptide chains consisting of different amino acids arranged in a unique sequence. Accordingly, two characteristic peaks arising from a C=O stretching vibration, at around 1630 cm$^{-1}$, and an N—H bending vibration, at around 1530 cm$^{-1}$, were observed, as shown in Figure 3(h).

In the case of 0 wt % and 5 wt % $Na_2CO_3$ solutions, the intensities of the peaks attributed to gelatin (1630 cm$^{-1}$ and 1530 cm$^{-1}$) were weak [Figure 3(b,c)], and gelatin formation on the paper surface was difficult. These results indicated that the 0 wt % and 5 wt % $Na_2CO_3$ solutions could not precipitate and fix gelatin on the paper surface by insolubilization of the gelatin hydrocolloid. The gelatin on the paper surface was not coacervated in the presence of these solutions and gelatin films or microcapsules were not formed.

In the case of 10 wt % $Na_2CO_3$, the FTIR peaks at around 1630 cm$^{-1}$ and 1530 cm$^{-1}$ confirmed that a gelatin film was formed on the paper surface [Figure 3(d)]. When the paper was prepared using 15 wt % or 20 wt % $Na_2CO_3$, the FTIR spectra showed the formation of gelatin microcapsules [Figure 3(e,f)]. The formation of gelatin microcapsules containing geraniol on the paper surface was caused by impregnation of the $Na_2CO_3$ coacervation agent.

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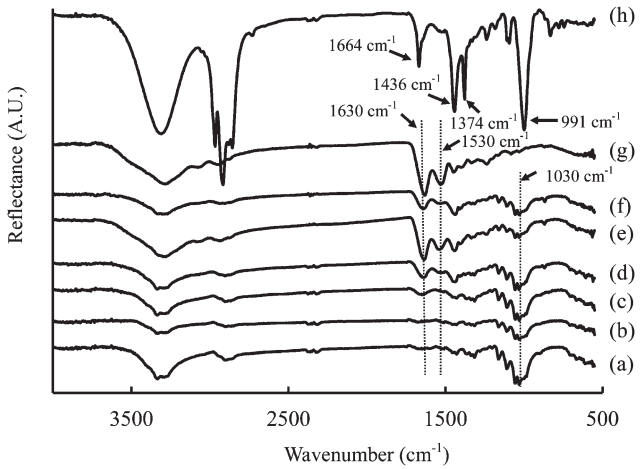


**Figure 3.** FTIR spectra of (a) filter paper before coacervation treatment, and of papers prepared using (b) 0 wt %, (c) 5 wt %, (d) 10 wt %, (e) 15 wt %, and (f) 20 wt % $Na_2CO_3$ solutions, (g) gelatin only, and (h) geraniol only.

In the case of 10 wt %, 15 wt %, and 20 wt % $Na_2CO_3$, the gelatin fixed on the paper surface was precipitated by addition of $Na_2CO_3$. When 10 wt % $Na_2CO_3$ was used, a gelatin film was formed, whereas microcapsules were formed when the concentration was 15 wt % or 20 wt %. The aqueous monomers adsorbed around the oil aggregated to form a microcapsule wall when the salt solution was added for coacervation of the aqueous monomer.[29] Mauguet et al. reported that when the salt solution for coacervation of the aqueous monomer was added very slowly, a microcapsule wall did not appear because the aqueous monomer adsorbed around the oil diffused into the emulsion mixture before aggregation of the aqueous monomer.[29] In our study, a similar phenomenon was thought to occur and the concentration of $Na_2CO_3$ affected the aggregation of the gelatin solution. In the cases of 15 wt % and 20 wt % $Na_2CO_3$, the gelatin previously adsorbed around the oil aggregated and formed a microcapsule wall. When 10 wt % $Na_2CO_3$ was used, the gelatin adsorbed around the oil was diffused into the emulsion mixture and gelatin microcapsules could not be formed. Impregnation of 10 wt % $Na_2CO_3$ therefore did not contribute to the formation of gelatin microcapsules and was insufficient to cause coacervation of gelatin fixed on the paper surface. These results suggested that the gelatin microcapsules were formed on the paper surface by coacervation of gelatin molecules fixed on the paper surface when the paper was impregnated with $Na_2CO_3$ solutions of high concentrations. The concentration of $Na_2CO_3$ solution used in impregnation of the paper was an important factor in the direct formation of gelatin microcapsules on the paper surface.

For $Na_2CO_3$ concentrations above 20 wt %, cracks were observed in the gelatin film formed on the paper surface, and fixation of the gelatin film was difficult because the thickness of the gelatin film was greater than about 10 $\mu$m. The optimal concentration of $Na_2CO_3$ was therefore 15 wt % or 20 wt %.

**Average Diameter of Gelatin Microcapsules and Mechanical Properties of the Paper Treated With Simple Coacervation Technique.** The average diameter of the gelatin microcapsules prepared using 20 wt % $Na_2CO_3$ was 3.81 $\mu$m [standard deviation (SD) = 1.65]. In the case of 15 wt % $Na_2CO_3$, the average diameter of the gelatin microcapsules was 1.57 $\mu$m (SD = 0.62). The particle size for 20 wt % $Na_2CO_3$ was larger than that for 15 wt % $Na_2CO_3$. This was thought to be the result of strong coacervation of the gelatin molecules on the paper surface caused by the high concentration of $Na_2CO_3$, as mentioned above.

The paper tensile strength before treatment was about 2.4 kN/m. The paper strength after the treatment was about 4 kN/m; the $Na_2CO_3$ concentration did not affect the paper strength. The paper strength was improved by physical bonding between the gelatin and the pulp.

**Effect of $Na_2CO_3$ Concentration on Geraniol Fixation**

Figure 4 shows the amounts of geraniol fixed on the paper surface; the amount increased with increasing $Na_2CO_3$ concentration. These results are in agreement with the results under these conditions for formation of gelatin microcapsules on the paper surface, i.e., geraniol was fixed on the paper surface by coacervation through impregnation of $Na_2CO_3$ solutions of high concentration, and was fixed by gelatin microcapsules formed on the paper surface. The formation of gelatin microcapsules was an important factor in the fixation of geraniol on the sheet surface. The fixation of geraniol on the paper surface by coacervation depended on formation of gelatin microcapsules on the paper surface.

The geraniol fixation amounts for papers prepared using 0 wt %, 5 wt %, and 10 wt % $Na_2CO_3$ solutions were 6.2, 7.2, and 8.2 g/m$^2$, respectively. These values were lower than that for the blank paper, 8.4 g/m$^2$. In the case of the blank paper, the geraniol could easily penetrate into the pulp fibers because of the low viscosity of the 0 wt % gelatin solution (0.9 mPa s at 25°C) compared with that of the 10 wt % gelatin solution (18 mPa s at 25°C). The geraniol was therefore fixed on the blank sheet by physical adsorption to the paper fibers.

The value for the blank paper was the same as those for papers prepared using 15 wt % and 20 wt % $Na_2CO_3$ solutions (8.9 g/

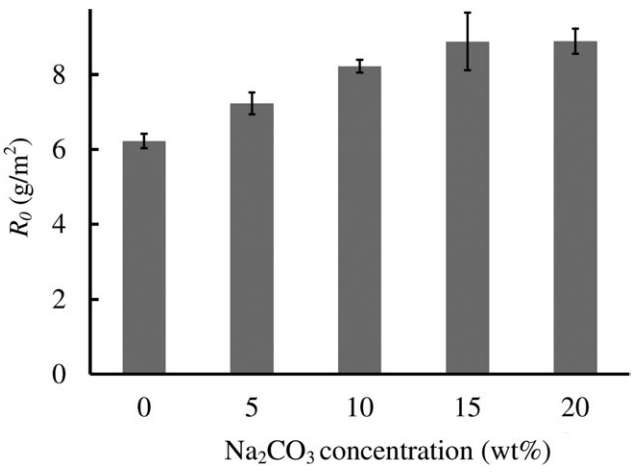


**Figure 4.** Effects of $Na_2CO_3$ concentration on the amount of geraniol fixed on paper.

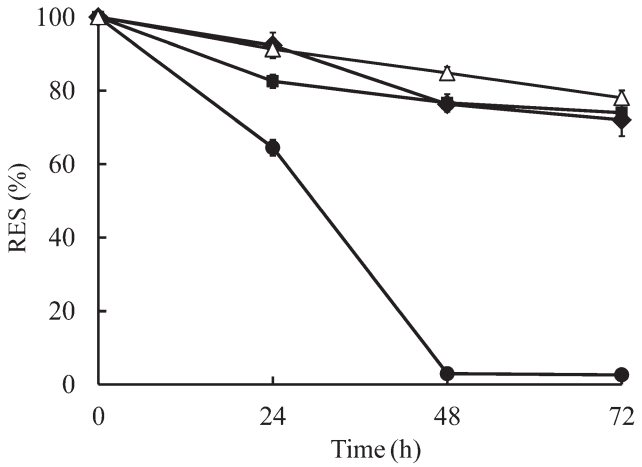


**Figure 5.** Residual geraniol for gelatin microcapsules prepared on (●) blank paper, (△) reference paper prepared using geraniol-$Ca(OH)_2$ composite powder and binder, and papers prepared using (■) 15 wt % $Na_2CO_3$ and (◆) 20 wt % $Na_2CO_3$.

$m^2$). Compared with the blank paper, smaller interstices, formed by the gelatin microcapsules, were available for geraniol adsorption and fixation on the prepared paper surface. These results indicate that the geraniol was not fixed by the filter paper, but by the gelatin microcapsules formed on the paper surface by coacervation.

In conclusion, the amounts of geraniol fixed on the paper surface depended on the $Na_2CO_3$ concentration. Conditions of 15−20 wt % $Na_2CO_3$ were used in subsequent experiments.

### Residual Amounts of Geraniol on Prepared Sheet and Sustained Release of Geraniol From the Sheet

The amounts of geraniol fixed on the prepared papers were the same as that for the blank paper, as mentioned above. However, the residual amounts of geraniol from the gelatin microcapsules prepared on the paper surface decreased at a slower rate than that from the blank paper (Figure 5). Geraniol was released from the pores of the gelatin microcapsules formed on the paper surface, and the gelatin microcapsules provided sustained geraniol release.

The RES of geraniol on the blank paper was 2.6% after 72 h, whereas the RESs of the papers prepared using 15 wt % and 20 wt % $Na_2CO_3$ solutions were 72% and 74%, respectively, after 72 h. The RES of the blank sheet reached almost 0% after about 144 h. For the papers prepared using 15 wt % and 20 wt % $Na_2CO_3$ solutions, the time for the RES to reach 0% was about 274 h. These results suggest that the blank paper could not provide sustained release of geraniol.

The RESs of geraniol on the papers prepared using 0 wt %, 5 wt %, and 10 wt % were 4.4%, 3.2%, and 64%, respectively, after 72 h. In the case of 0 wt % and 5 wt % $Na_2CO_3$, the RES values were almost the same as that of the blank sheet because a gelatin film or microcapsules were not formed. The geraniol was adsorbed on the outside of the gelatin film formed on the paper prepared using 10 wt % $Na_2CO_3$, so the RES after 72 h was smaller than those obtained using 15 wt % and 20 wt % $Na_2CO_3$. In the cases of 15 wt % and 20 wt % $Na_2CO_3$, the geraniol was fixed inside the gelatin microcapsules. These phenomena depend on the formation processes of the gelatin film and microcapsules, as mentioned above. The papers coated with gelatin microcapsules therefore provided sustained release of geraniol. These results showed that the gelatin microcapsules on the paper surface gave a sustained-release function.

In the case of the reference paper prepared using the geraniol-$Ca(OH)_2$ composite powder and a binder, the RES of geraniol was 78% after 72 h. These results indicated that the paper prepared by coacervation had a comparable function to that of the reference paper. However, preparation of the reference paper consisted of two steps: preparation of the geraniol powder and coating using a binder. The coacervation technique was therefore more efficient than the usual methods.

Control of the RES by varying the $Na_2CO_3$ concentration was difficult because the wall thicknesses of the gelatin microcapsules prepared using 15 wt % and 20 wt % $Na_2CO_3$ solutions were the same (about 6 $\mu$m), so the RESs of these papers were the same.

Preparation of gelatin microcapsules on the paper surface by coacervation eliminated the need for a microencapsulation process and a binder, and provided better sustained release of geraniol than that obtained with the blank paper. These results indicate that this technique was effective for producing paper capable of sustained release of geraniol.

## CONCLUSION

Gelatin microcapsules containing geraniol were formed directly on paper, without a binder, by simple coacervation when 15 wt % and 20 wt % $Na_2CO_3$ solutions were used for impregnation of paper treated with an O/W emulsion of gelatin containing geraniol. However, gelatin microcapsules were not formed when 0 wt %, 5 wt %, and 10 wt % $Na_2CO_3$ were used. Impregnation with high-concentration $Na_2CO_3$ produced coacervation of the gelatin molecules fixed on the paper surface. Gelatin microcapsules were not formed at low concentrations of $Na_2CO_3$ because coacervation of the gelatin molecules fixed on the paper surface did not occur.

Geraniol retention reached a maximum value (8.9 g/$m^2$) in the case of 15 wt % and 20 wt % $Na_2CO_3$ solutions. The formation of gelatin microcapsules was important for geraniol fixation. The direct preparation of gelatin microcapsules on the paper surface affected the sustained release of geraniol. The RESs of gelatin microcapsules prepared using 15 wt % and 20 wt % $Na_2CO_3$ solutions were higher than those of a blank sheet and the papers prepared using 0 wt %, 5 wt %, and 10 wt % $Na_2CO_3$.

Gelatin microcapsules containing geraniol, prepared directly on a paper surface, without using a binder, were used to produce a functional paper.

## ACKNOWLEDGMENTS

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