J. Soc. Cosmet. Chem., 22, 655–666 (September 17, 1971)

Encapsulated Perfumes in Aerosol Products

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Presented May 26–27, 1970, New York City

Synopsis—Stable, spray-dried, ENCAPSULATED FRAGRANCES which are formulated in AEROSOLS are described. When sprayed on a surface, under both *in vivo* and *in vitro* conditions, these gradually release fragrance upon exposure to moisture. It is shown that RELEASE RATE can be varied according to the liquid vehicle and that it varies with the individual test subject and the stimuli to which he is exposed.

A novel analytical technique has been developed that simultaneously monitors the volatiles relcased from an encapsulated fragrance and the moisture content of the axillary region of the subject.

Introduction

Liquid fragrances used in aerosol products tend to behave in the same manner as topically applied perfumes. The odor of the more volatile perfume components is noticed first, that of the moderately volatile components next, and at the end of a period of time only the odor of the least volatile ones. This effect is characterized in Fig. 1 by the bolder curves.

Both the strength and character of a liquid fragrance change within a time period. Ideally, freshness of top note and unfading odor strength should be maintained throughout the application life. Fulfillment of such a requirement is not possible at present with liquid perfume oils. However, if the release of perfume volatiles could be delayed by a suitable encapsulation until functionally needed, greater fragrance integrity and

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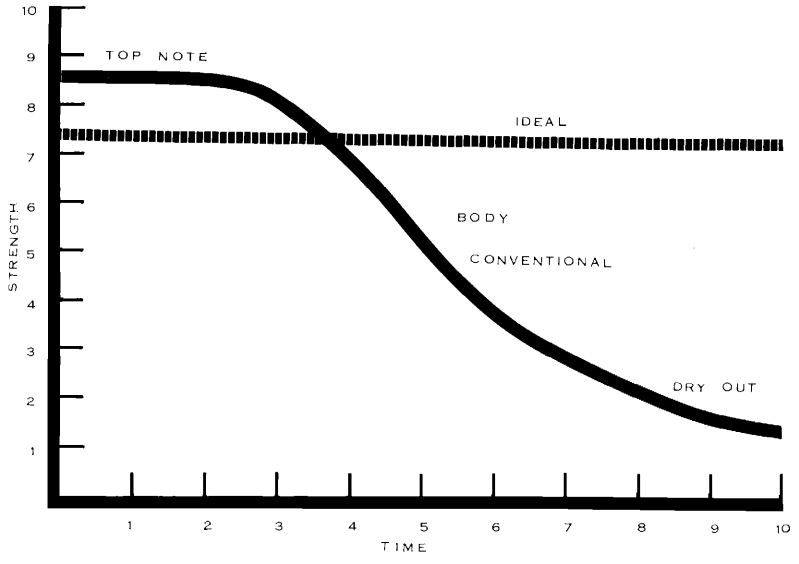

Figure 1. Comparison of ideal perfume behavior with actual effect

more uniform strength could be provided, which would approach the ideal shown in Fig. 1. Highly water-soluble encapsulations of perfume oil are one approach to producing a delayed and periodic fragrance release in a properly formulated aerosol product (1).

Spray drying is one approach to producing such an encapsulation (2). By this method, free-flowing powders with up to 50% perfume oil in a highly water-soluble shell have been produced utilizing our technology.

The encapsulations may be typified as dried, particulate, micellar structures containing perfume oils. Since the encapsulation particles consist of one or more dried micelles, the finished powder has a particle size distribution which reflects this characteristic. Table I shows the particle size distribution of one such product, (IN) -CAP®.*

Experimental

Initial small-scale, valve clogging studies were undertaken to determine physical compatibility with aerosol systems. These were supplemented by large-scale tests† in an aerosol, dry antiperspirant formulation. These tests indicate a cloggage level that is not greater than the controls.

* (IN) -CAP is a registered trademark for water-soluble, encapsulated perfumes manufactured by Polak's Frutal Works, Inc., Middletown, N. Y.

† Carried out in cooperation with Aerosol Techniques, Inc., Milford, Conn.

Table I

Typical Particle Size Distribution of (IN)-CAP

	Per Cent
Through 200 mesh	99
Through 230 mesh	97
Through 270 mesh	80
Through 325 mesh	70

Once the physical compatability properties had been determined, attention was focused on the performance of the encapsulations. From the onset of the project the services of perfumers were employed to evaluate the odor-release characteristics of the encapsulatd perfume in various products over a period of time. In addition, perfumed, aerosol antiperspirant samples were also provided for subjects who were questioned carefully as to their observations after extended usage. Although the subjective assessment of the functionality of the encapsulated perfume was convincing, a more objective means to measure the fragrance release of the encapsulated perfume both *in vivo* and *vitro* was sought.

An analytical procedure was developed based on gas-liquid chromatographic analysis of vapor samples withdrawn from treated areas. Considerable difficulty was initially encountered with quantitative determinations because of the large variety of materials present in the normal perfume composition. The vapor pressures and the concentrations of most chemicals used in perfumes are too low for accurate quantitative detection in a small vapor sample. Therefore, materials were chosen for encapsulation that have a high enough vapor pressure to make detection and measurement relatively easy. An additional requirement of rapid elution in the gas chromatograph to enable us to perform an analysis every 15 min is fulfilled by these high-vapor-pressure materials.

A representative selection of materials was made from those commonly found in perfume compositions. This selection included hydrocarbons, alcohols, esters, and ethers. The encapsulation of these single materials was identical to the encapsulations of normal perfume compounds containing multiple components. These encapsulations were incorporated in a representative aerosol antiperspirant product made according to the formulation in Table II. This formulation provides a net 1% level of encapsulated perfume in the finished can, which represents the highest levels of encapsulated perfume tested. When lower levels were used, the balance was made up with isopropyl myristate.

Table II
Antiperspirant Formulation

Concentrate	Per Cent by Weight
1. Isopropyl myristate[a]	55.45
2. Cab-O-Sil M-5[b]	3.64
3. Aluminum chlorhydrate[a]	31.82
4. (IN)-CAP perfume[c]	9.09
Fill	
Concentrate	11.00
Propellants (50:50) 11/12	89.00

[a] Wickhen Products, Inc., Huguenot, N. Y.
[b] Cabot Corporation, Boston, Mass.
[c] Registered trademark of Polak's Frutal Works, Inc., Middletown, N. Y.

Figure 2. Sampling device and syringe

Control samples were also prepared using corresponding unencapsulated liquid materials in the same formulation. Depending upon the specific vapor pressure of the material involved, a variety of dosages were

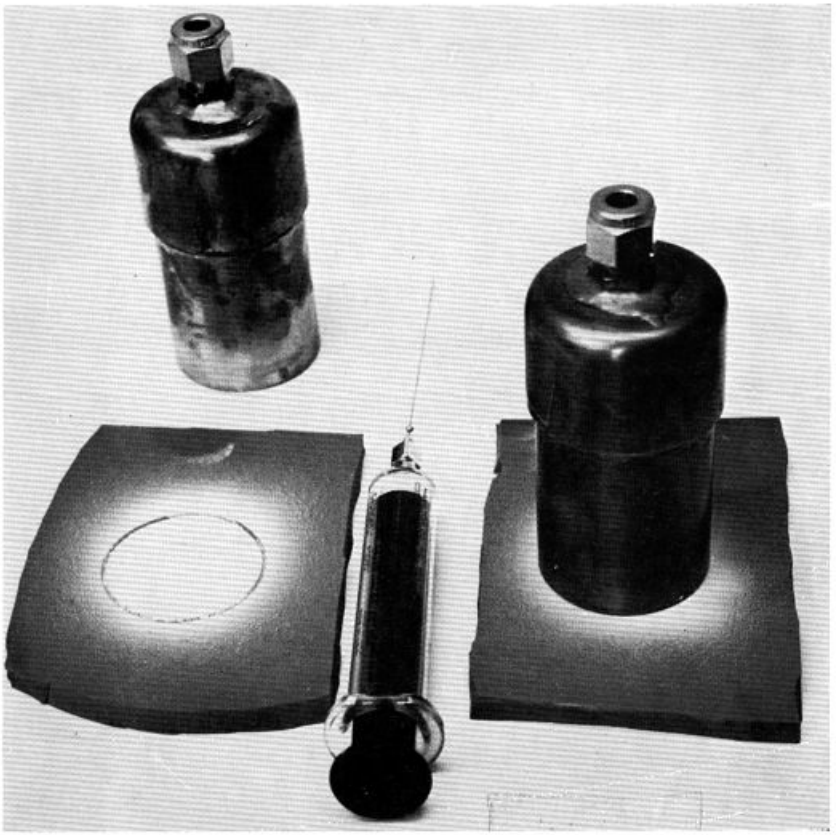

Figure 3. In vitro sampling apparatus

used in the finished aerosol samples. (These dosages ranged from 0.4 to 1.0% for the encapsulation with an equivalent range of 0.2 to 0.5% for the unencapsulated oil.) Aerosol samples, prepared as previously described, were applied to either silicone rubber pads, for *in vitro* tests, or to the axillary region of a human subject, for *in vivo* tests.

A sampling device was developed to entrap the perfume vapors above the axillary region consisting of a copper cylinder, $1^1/_2$ in. in diameter and 3 in. long, with a silicone septum at the closed end, and having a volume of 100 cc (Fig. 2). In practice, the open end of the cylinder is placed over the tested region for 60 sec, as shown in Fig. 3, and then a vapor sample is withdrawn into a 10-cc gas-tight hypodermic syringe equipped with a 3-in., No. 22 needle, also shown in Fig. 2.

A 3-ft, $^1/_4$-in. o.d. copper column filled with 2.0% Apiezion M* on 60

* Apiezion M is available from James G. Biddle Co., Plymouth Meeting, Pa.

to 80 mesh Chromosorb W* is used at a temperature of 150°C and a helium flow rate of 80 cc per minute. In order to achieve maximum sensitivity, a flame ionization detector is employed. The 10-cc vapor sample is mostly air which causes extinction of the flame in the detector. The latter has to be reignited for each sample. The relative concentration of the organics in the vapor sample is determined by measuring its peak height.

During the course of a particular test it is necessary to have the subject perspire in order to release the perfume. This is best accomplished by "heating" the subject with the aid of an electric blanket and sitting on an electric heating pad. The sipping of hot tea by the subject also facilitates perspiration.

Another technique, again based upon gas-liquid chromatography, was developed in order to measure water vapor caused by the perspiration of the subjects. A 3-ft, $^1/_4$-in. o.d. copper column with 50% Carbowax 20M† on 60 to 80 mesh Chromosorb W is used with a helium flow rate of 10 cc per minute at 130°C. The unusual 50% substrate is a development that allows water vapor to be quantified since it gives symmetrical peaks. The high liquid ratio lessens adsorption phenomena. A thermal-conductivity detector is used since the hydrogen flame detector is insensitive to water vapor.

The same sampling device is used and again it is allowed to equilibrate for one minute in the axillary region. A 10-cc sample is taken, again utilizing a gas-tight hypodermic syringe.

The water vapor in the air due to atmospheric humidity gives us a background reading. As the subject perspires, the water vapor reading obtained in the gas chromatograph increases to a maximum. After the subject perspires for a given time and cooling is desired, the electric blanket and electric heating pad are removed. A marked reduction in the axillary water vapor is subsequently observed.

Results and Discussion

The purpose of the analytical procedure was to obtain objective, quantitative data on the performance of encapsulated perfumes in aerosol products. Our original olfactive observations described the performance of the encapsulated perfumes as having sustained release, delayed release, and maintainence of freshness.

The initial *in vitro* tests confirmed that repeated release of volatiles from the encapsulated perfume did occur. The results shown in Fig. 4

* Chromosorb W is available from Analabs, Inc., Hamden, Conn.

† Carbowax 20M is available from Union Carbide, New York, N. Y.

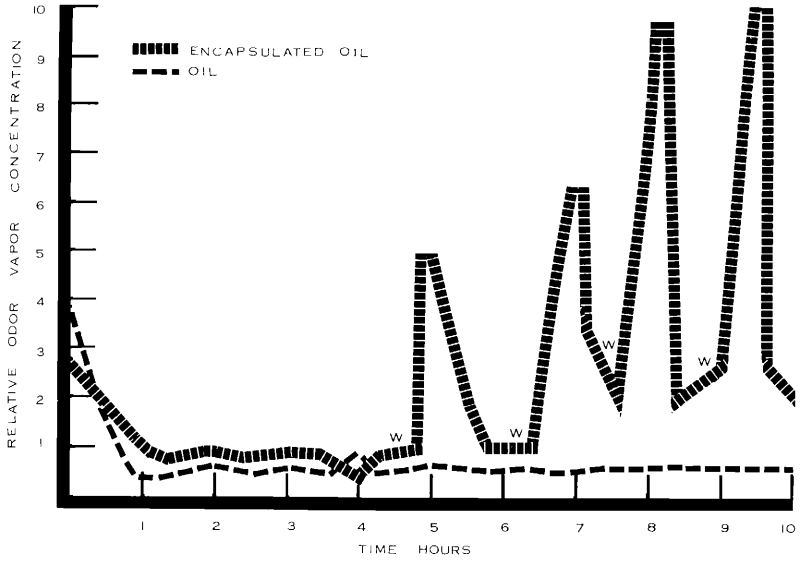

Figure 4. Moisture-induced fragrance release

are typical of those obtained in the *in vitro* tests. Moisture in the *in vitro* tests was applied by spraying a mist from an atomizer onto the test area. The *W*'s indicate the points at which moisture was applied. Time was allowed to elapse before the first wetting so that some of the IPM in the product could be absorbed by the silicone rubber pads. Sufficient moisture was applied to form a visible film of water. These tests were repeated, *in vivo,* and similar results were obtained.

The subjects were artificially heated at the points, *P,* to promote perspiration in an attempt to simulate the results of normal activity at various times. Tests were then conducted seeking a correlation that might be found between the composition of the aerosol formulation and the degree of release, at any given time, of the encapsulated perfume. The comparison of moisture vapor and fragrance release curves shows the close correlation of the perspiration to the release of volatiles (Fig. 5).

Substitutions were made for a portion of the isopropyl myristate in the original formulation. A variety of nonpolar materials was chosen on the basis of their compatibility with the encapsulation. Samples were prepared as shown in Table III. These samples were then subjected to *in vitro* testing. The results of these tests confirmed the correlation between the aerosol formulation and the susceptability to moisture of highly water-soluble materials, such as the fragrance encapsulations which are dispersed in nonpolar aerosol systems (Fig. 6).

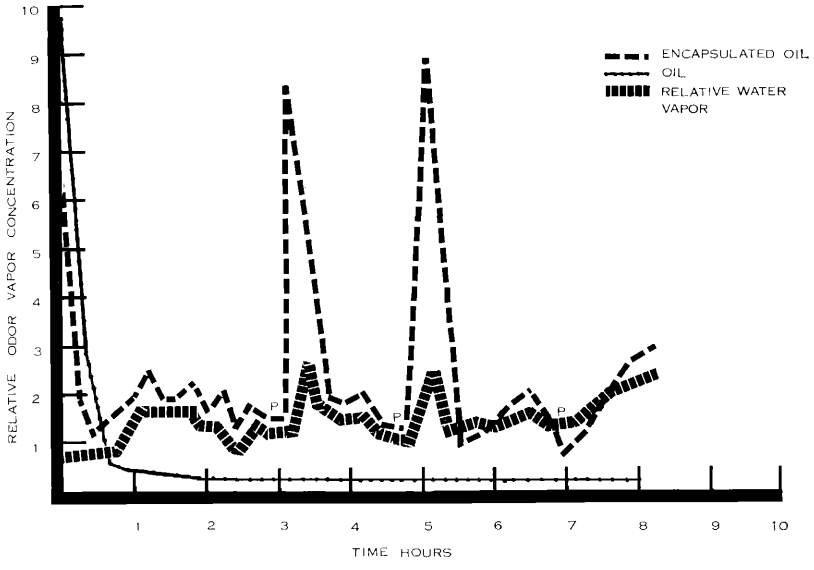

Figure 5. Perspiration-induced fragrance release

Table III
Modification of Antiperspirant Bases

Concentrate	Formulas[g]			
	1	2	3	4
Isopropyl myristate[a]	55.5	27.7	27.7	27.7
Robane[b]	...	27.7	...	...
Mineral oil[c]	...	...	27.7	...
Polylan[d]	...	...	...	27.7
Cab-O-Sil[e]	3.6	3.6	3.6	3.6
Aluminum chlorhydrate[a]	31.8	31.8	31.8	31.8
(IN)-CAP perfume[f]	9.1	9.1	9.1	9.1
Fill				
Concentrate				11.0
Propellants (50:50)				89.0

[a] Wickhen Products, Inc., Huguenot, N. Y.
[b] Robeco Chemicals, Inc., New York, N. Y. (hydrogenated squalene).
[c] Witco Chemical Co., New York, N. Y.
[d] American Cholesterol Products, Inc., Edison, N. J. (polyunsaturated liquid esters).
[e] Cabot Corporation, Boston, Mass. (coloidal silicone dioxide).
[f] Registered trademark of Polak's Frutal Works, Inc., Middletown, N. Y.
[g] Formula No. 1 was the control as used in all of the testing. Formulas No. 2, 3, and 4 are 50% replacements of the IPM with the various nonpolar materials.

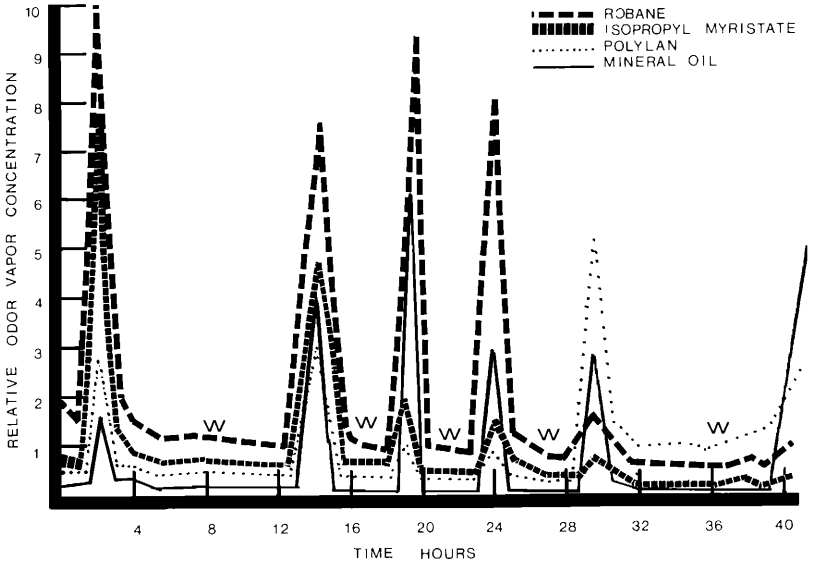

Figure 6. Fragrance release as function of polarity of vehicle

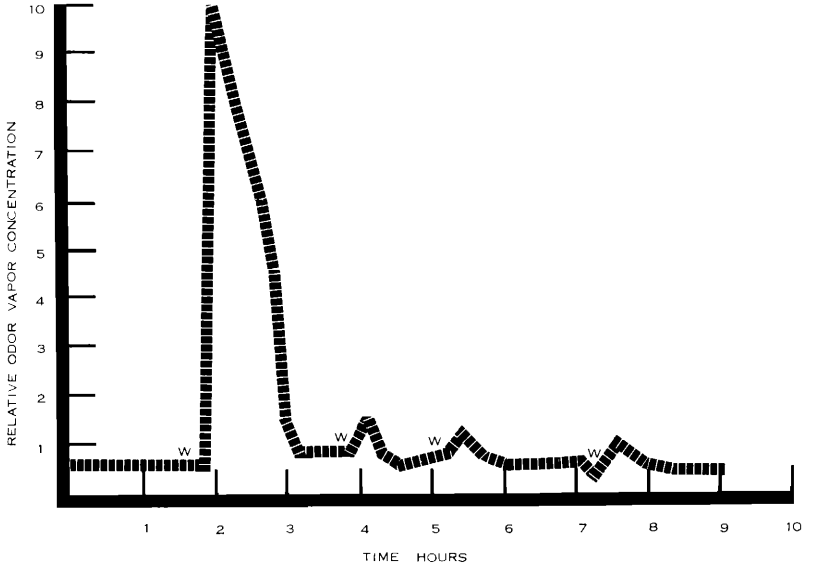

Figure 7. Fragrance release in absence of vehicle

A test was run using encapsulated perfume only to show the effect of the absence of nonpolar vehicles, such as IPM. The results are shown in Fig. 7. The contrast between Figs. 6 and 7 indicates that the nature of the aerosol vehicle accounts for the perfume release characteristic of the

aerosol product. In Fig. 7, it is noted that even though release does occur each time the sample is wetted, the subsequent releases are nominal in comparison to the first.

No attempt was made to determine whether or not the formulation changes shown in Table III also affect the release of the aluminum chlorhydrate. It may be postulated, however, that these changes would affect any dispersed, water-soluble material in the aerosol formulations. We retained the IPM-based aerosol, antiperspirant formulation for the remaining tests.

A number of successive tests were run on a small sample of human subjects of both sexes. It was attempted to establish the range of release characteristics that might be encountered in a broader sampling of subjects. This was accomplished by increasing or decreasing the subject's perspiration rate artificially (Fig. 8). In addition, subjects were chosen who represented a considerable difference in normal perspiration rate. Figures 9 and 10 show the variations between two subjects using the same aerosol antiperspirant formulation and encapsulated perfume. Figure 9 shows that the particular subject perspired considerably even before heat was applied, as indicated by the letter, *P,* at the 5-hour mark. Nevertheless, release still occurred after 8 hours.

It is noted that even though considerable variation does occur from subject to subject repeated release is evident in each case. This demon-

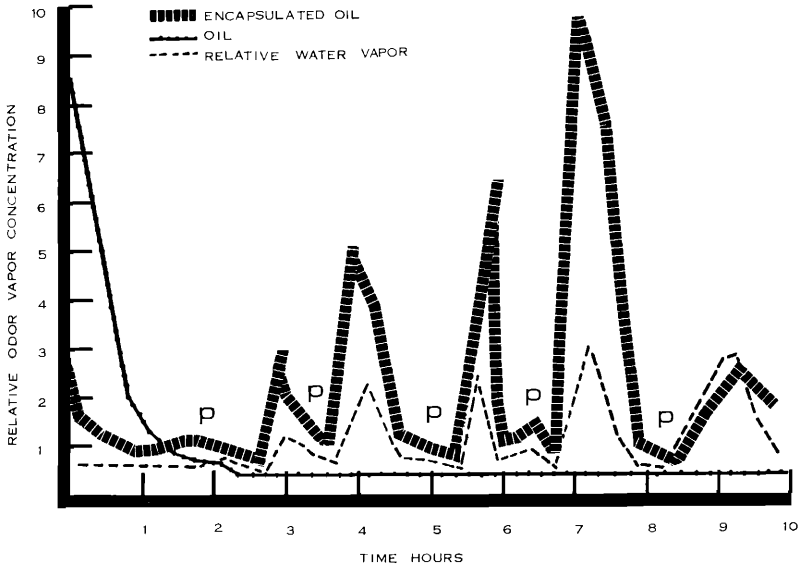

Figure 8. Fragrance release by induced perspiration

strates that the delayed and gradual release of perfume in aerosol products can be realized. Antiperspirant products could probably be formulated to fulfill specific time-release requirements as well as for subjects

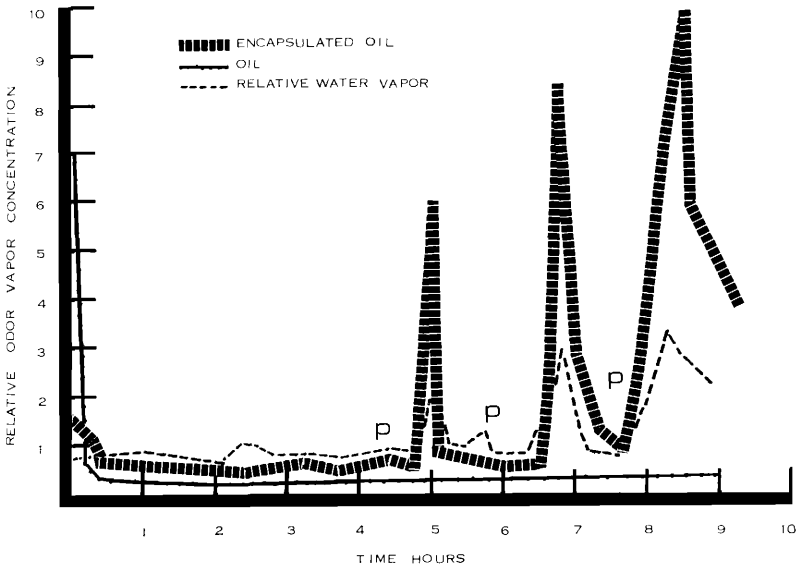

Figure 9. Fragrance release with calm subject

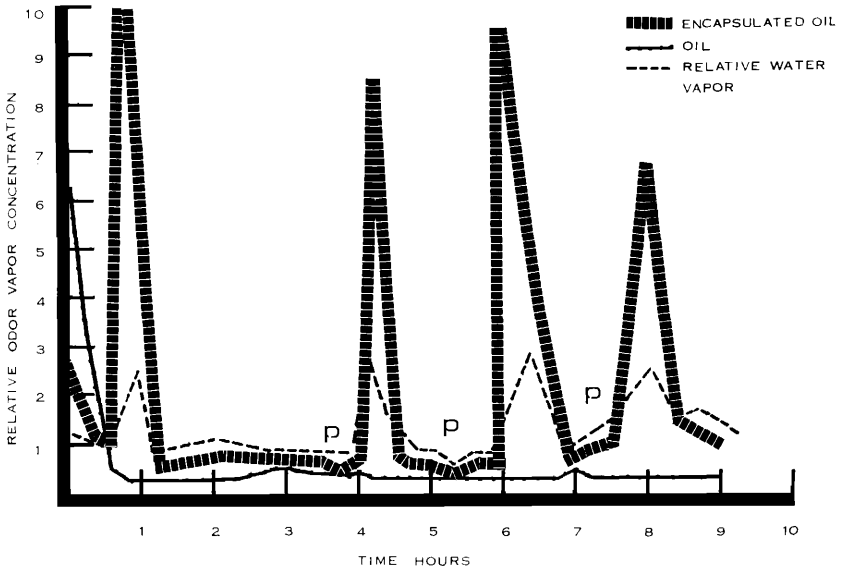

Figure 10. Fragrance release with nervous subject

with moderate, heavy, or light perspiration by varying the particular nonpolar vehicle used in the formulation.

The same delayed and gradual release has been incorporated into other aerosol products, such as feminine deodorant sprays, foot sprays, etc. (3). The same encapsulation system is also capable of incorporating other materials along with perfume oils. Encapsulated perfumes have been prepared with perfume oil to which has been added either hexachlorophene; an oil-soluble, germicidal quaternary; or undecylenic acid. In general, oil-soluble, nonpolar materials compatible with the perfume ingredients may be incorporated in the encapsulations along with the perfume oil so that they also release over a period of time.

A wide variety of fragrance types have been successfully encapsulated. However, adjustments are sometimes necessary in the perfume formulation to ensure accurate reproduction of the released perfume oil in the encapsulated form. With these encapsulations it is possible to include perfume types in product formulations which would not otherwise be suitable. Fragrance types, with very volatile character that would not be long lasting enough for inclusion in a product as liquids, can be successfully employed using encapsulated perfumes.

The encapsulated perfumes in aerosol formulations have been tested for extended periods of time with positive results. In the aerosol antiperspirant formulations used in most of our testing, we ran elevated-temperature-stability tests at 130°F for 14 months. These tests showed that both the release characteristics and fragrance character of the encapsulated perfume oil were maintained even though the small amount of surface oil on the encapsulations had broken down.

It is concluded that a stable and functional encapsulated perfume for use in aerosol products can be produced. The technology developed also provides for other new product possibilities and helps solve problems that previously had no solution. A novel analytical method has also been developed to measure the rate of perfume release as well as moisture release in the axillary region.

(Received February 10, 1971)

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(2) Report by the Graduate Students at the Harvard Business School, *Microencapsulation*, Management Reports, 1963, p. 72.

(3) Bakan, Joseph A., Paper on microencapsulation presented to the Eastern Regional IPT Section of the Academy of Pharmaceutical Science, Philadelphia, Pa., October 4, 1968.