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Development of a novel hybrid powder formulated to quench body odor

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Synopsis

Olfactory and instrumental analyses show that short-chain fatty acids contribute to both foot and axillary malodors.

The mechanism of choice to quench short-chain fatty acid malodors was to convert volatile short-chain fatty acids into their corresponding nonvolatile odorless metallic salts. Several metal-containing candidates were evaluated by means of headspace gas chromatography (HS-GC) for their ability to efficiently quench short-chain fatty acids. Zinc oxide was found most suitable for this purpose. Despite its strong deodorizing power, due to its aggregating ability, shortcomings such as clogging of aerosols and rough texture are unavoidable when formulating zinc oxide into deodorant products of various forms. By forming a hybrid powder in which zinc oxide is uniformly covered on the surface of a spherical resin such as nylon, these shortcomings were overcome without sacrificing any deodorizing power.

Body odor quenchers formulated with this hybrid powder were more efficacious than conventional antiperspirants and deodorants on both foot and axillary odor.

INTRODUCTION

Regardless of sex, age, or race, people have always been sensitive in trying to eliminate offensive body odors as much as possible. To fulfill such demands, countless products by various manufacturers have appeared in the marketplace. Human body odors result from interactions between secretions of eccrine, sebaceous, and apocrine glands, and resident bacteria. Several approaches have been made to control body odors, out of which the antiperspirants and antimicrobials have been most successful. Antiperspirants inhibit perspiration by means of aluminum salts, and antimicrobials inhibit odor-forming bacteria. Nevertheless, such ingredients are intended to prevent the generation of body odors and generally have little effect in reducing malodor once formed.

Body odors have been investigated in terms of chemical compound constituents by dermatologists and analytical chemists, but little is still known as to which chemical compounds are responsible for the malodor for specific body sites. We have recently reported that short-chain fatty acids contribute considerably to both foot and axillary odor (1). Especially in the case of foot odor, isovaleric acid was found to be the key odor component responsible for the malodor. As for axillary odor, a particular key odor component remains yet to be identified, although short-chain fatty acids of comparatively long carbon chain (>C6) seem to comprise a considerable portion of the malodor. It is well known that the method of choice in eliminating short-chain fatty acid malodors is to convert volatile short-chain fatty acids into their corresponding odorless nonvolatile fatty acid metallic salts.

In this study, ingredients capable of converting short-chain fatty acids into their metallic salts were investigated by headspace gas chromatography (HS-GC). Furthermore, deodorant products formulated with such ingredients, which hopefully will not only prevent but also act directly upon malodor already formed, were compared with conventional products for their ability to efficiently quench foot and axillary odor.

EXPERIMENTAL

HEADSPACE GC ANALYSIS FOR EVALUATING QUENCHING ACTIVES

Equilibrium headspace gas chromatography was employed to assess the ability of various compounds to efficiently quench short-chain fatty acids. HS-GC is unique in that only the vaporized portion of the sample is introduced into the GC. The method permits analysis of volatile chemicals without having to introduce the total sample matrix into the GC. The sample matrix may well contain nonvolatile compounds that are neither amenable nor desirable for GC operation. Isovaleric acid was chosen to represent the short-chain fatty acids since it was found to be the key odor component of foot odor and also because of its extremely low olfactory threshold level (2). Quantitative comparison among the candidates should easily be made since the concentration of isovaleric acid in the vapor phase should be directly proportional to the GC peak area obtained.

Approximately 80 mg of the candidate was accurately weighed in a glass vial especially designed for the headspace gas chromatograph, to which one ml of 0.5% isovaleric acid aqueous solution was added. The vial was tightly closed and placed inside an ultrasonic generator for five minutes for sample dispersion. It was then placed inside an oven maintained at 60°C for 60 minutes to allow isovaleric acid vapor to equilibrate in the headspace of the vial prior to analysis.

The vial was introduced into a Perkin Elmer SIGMA 3B headspace gas chromatograph equipped with a flame ionization detector and a three-foot glass column packed with 10% FFAP. The HS-GC was operated at a column temperature of 150°C isothermally. The headspace of the vial was automatically pressurized for four minutes, after which it was forced into the carrier gas flow. The GC peaks were recorded and the peak area was calculated in arbitrary units using a Hewlett Packard HP 3380A integrator. For each candidate, three consecutive GC runs were acquired, and the mean peak area was employed for the calculation explained later on. To check the stability of the GC, the standard isovaleric acid aqueous solution was measured once in every five sample runs.

Each candidate was evaluated by calculating a value expressed as "isovaleric acid consumption/mg ingredient." An example of how to calculate the isovaleric acid consump-

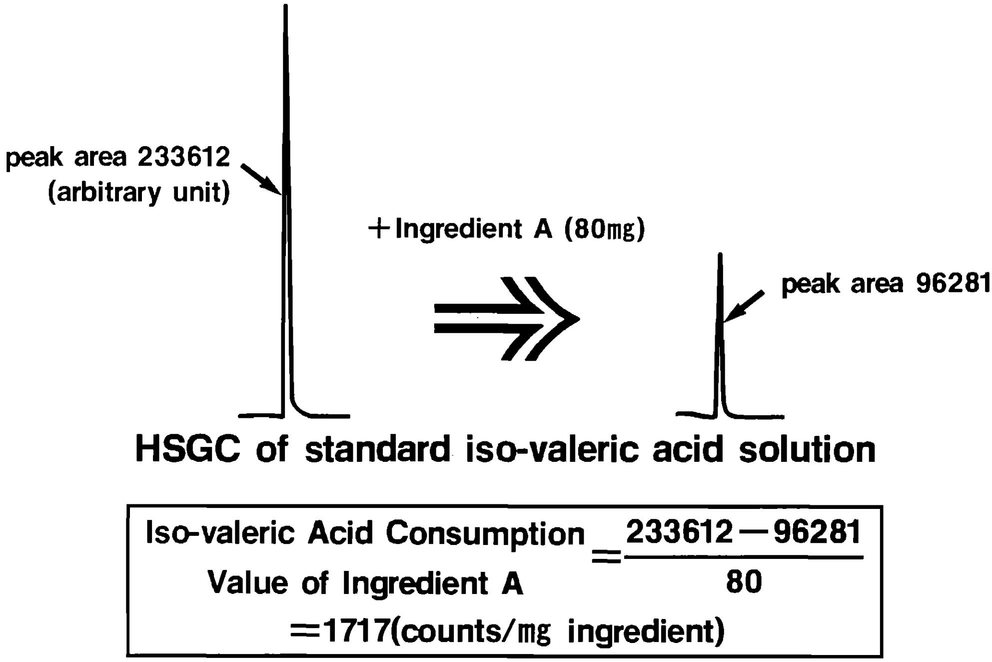

Figure 1. Calculation of isovaleric acid consumption values. Upon addition of a quenching ingredient, the GC peak area of the standard isovaleric acid solution decreases.

tion value is shown in Figure 1. The larger the value, the greater the efficacy of the ingredient to quench isovaleric acid odor.

CONFIRMATION OF THE QUENCHING MECHANISM BY FT-IR

Fatty acids in the free form and metallic salt form are readily distinguishable by Fourier transform infrared spectrophotometry (FT-IR), since they exhibit characteristic absorption bands at different wave numbers. Therefore, the speculated quenching mechanism in which volatile short-chain fatty acids are converted into metallic salts was confirmed by FT-IR. To a mixed aqueous solution (0.1%) of propionic, isovaleric, and caproic acids, resembling that of a sweaty body malodor, zinc oxide was gradually added until excess zinc oxide started to precipitate. The excess zinc oxide was filtered, and the filtrate was evaporated to dryness in vacuum. An FT-IR spectrum of the resulting residue in the form of a KBr tablet was acquired using a Biorad Qualimatic FT-IR, scanning a range of 4000 to 400 cm^{-1}.

FORMATION OF A ZINC OXIDE/NYLON HYBRID POWDER

Although zinc oxide is a widely used cosmetic ingredient, it possesses a couple of unfavorable shortcomings that derive from its aggregating property. Even though some commercially available zinc oxides are claimed to be as small as 0.1 μm in particle size, they readily cohere to form massive lumps, as shown in Figure 2. This is said to be due to the electrostatic behavior of zinc oxide, and can thus easily lead to clogging of aerosol

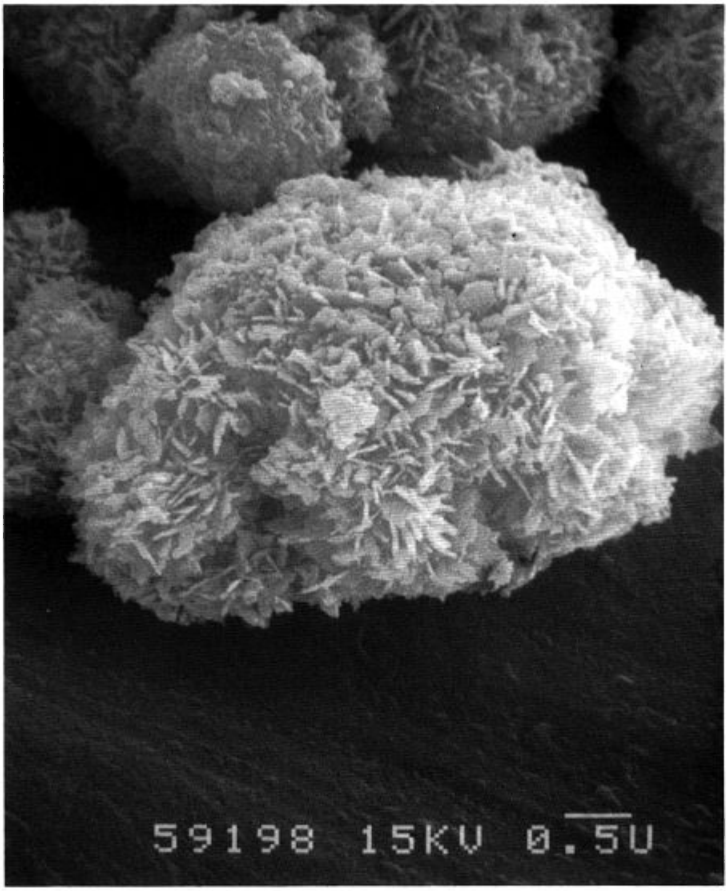

Figure 2. Photomicrograph of fine particle size (0.1 μm) zinc oxide. The zinc oxide particles aggregate to form a massive lump.

products. It also has a fairly rough texture, which may feel uncomfortable when applied to sensitive skin. The whiteness of zinc oxide is often considered too vivid in contrast to skin color and may be emphasized when applied to exposed parts of the body. To overcome such shortcomings, we attempted to form a composite or "hybrid" powder,

Table I
Formulae of Body Odor Quenchers

	Formula			
Ingredients	1	2	3	4
AHC	0	0	30	30
Talc	50	50	35	50
ZnO/nylon (20%)	0	30	15	0
ZnO	30	0	0	0
S. microbeads	20	20	20	20

The content of each ingredient in the powder is shown in weight percent.

which consists of a spherical nylon as the core powder, the surface of which is uniformly covered with fine-particled zinc oxide. To 80 parts of nylon 12 powder (average particle size 6.6 μm, Nikko Rica Corp.), 20 parts of zinc oxide (average particle size 0.1 μm, Sakai Kagaku Kogyo) were added and mixed together in a Henschel mixer (Mitsui Miike Machinery Co., Ltd., Model 10B) for five minutes. The mixture was placed inside a tumbling mill (Retsch, Model S2) charged with alumina balls (0.8–30 mm i.d.), where it was mixed and compressed for 30 to 60 minutes.

EFFICACY OF QUENCHERS FORMULATED WITH HYBRID POWDER ON FOOT ODOR

Efficacy of body odor quenchers in the form of aerosols was assessed. Four quenchers, whose powder parts formulae are shown in Table I, were prepared for the assessment. Our panel consisted of six subjects (six men, 20 to 30 years old) with fairly strong foot odor, all from our laboratory. For each formula the assessment was carried out in the following manner.

First of all, the six subjects self-evaluated their right and left feet, based on a five-step foot odor intensity: 0, no foot odor; 1, faint foot odor; 2, medium foot odor; 3, strong foot odor; 4, extremely strong foot odor.

After evaluation, the quencher was applied to the foot possessing the stronger foot odor, and the other foot was left untreated. The quencher was always applied only on the former foot during the assessment, and the latter was left as control. The quencher was applied twice a day for two days. Foot odor was self-evaluated just before applying the quencher. An example of such an assessment procedure is shown in Figure 3. As shown

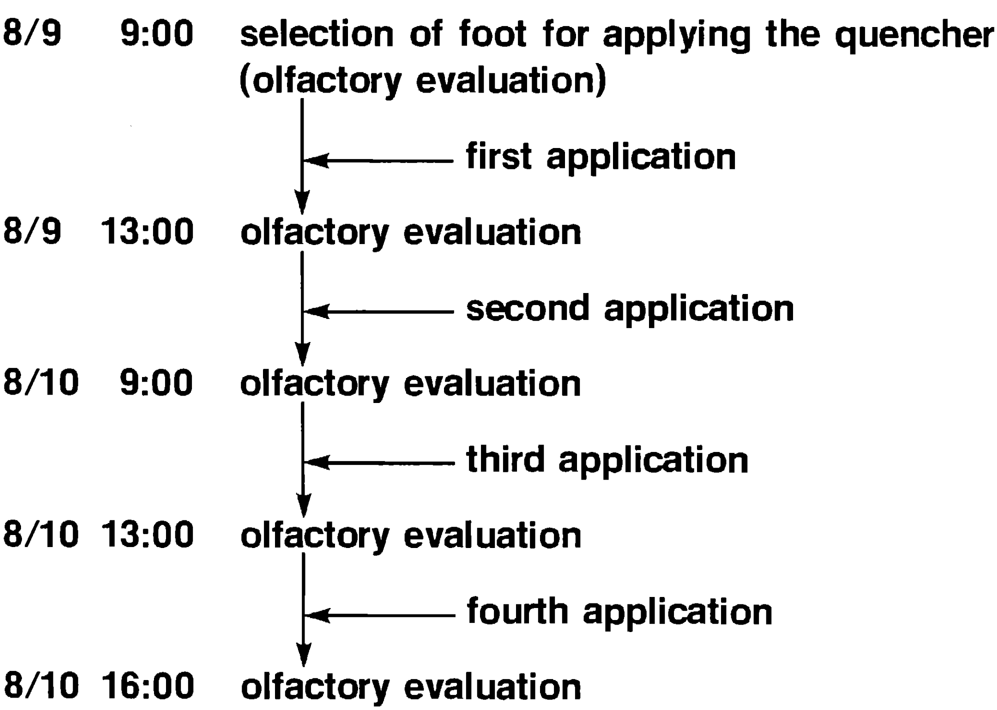

Figure 3. Assessment procedure for body odor quenchers on foot odor. The assessment lasts for two days during which four applications and five evaluations are accomplished.

in the figure, foot odor was evaluated five times during an assessment. During the two days, the subjects were allowed to bathe but not permitted to use soaps or deodorants of any kind. The same assessment was carried out on all four formulae.

EFFICACY OF QUENCHERS FORMULATED WITH HYBRID POWDER ON AXILLARY ODOR

Efficacy of quenchers formulated with hybrid powder was assessed on axillary odor as well. A panel of 20 patients (three men, 17 women, average age 30), suffering from strong axillary odor, was selected from hospitals and universities in Japan. Double-blind trials were made on body odor quencher A (a conventional formula containing aluminum chlorhydrate as active ingredient + hybrid powder, equivalent to formula 2) and body odor quencher B (a conventional formula containing only aluminum chlorhydrate as active ingredient, equivalent to formula 4). Trained olfactory assessors evaluated the efficacy of A and B as listed below:

Efficacy of A $>>$ efficacy of B
Efficacy of A $>$ efficacy of B
Efficacy of A $=$ efficacy of B
Efficacy of A $<$ efficacy of B
Efficacy of A $<<$ efficacy of B

Quencher A was applied to the right axilla and B to the left, or vice versa. The quenchers were applied twice a day, once in the morning and once in the afternoon, for seven consecutive days during which the patients could bathe, but the usage of neither soaps nor deodorants was permitted. The axillae of the patients were evaluated by the assessors on the seventh day. The identity of A and B was kept blind to both the patient and the assessor, and only the supervisor who finally collected the results could distinguish the two formulae.

RESULTS AND DISCUSSION

HEADSPACE GC ANALYSIS FOR EVALUATING QUENCHING ACTIVES

If we keep in mind the quenching mechanism we are proposing here, the candidates under investigation should contain metallic elements, preferably with a mild alkaline effect, and needless to mention, must be safe on human skin. Several possible candidates to fulfill the above demands were analyzed by headspace GC. Isovaleric acid consumption values of the candidates are illustrated in Figure 4. Fine-particled zinc oxide was found to be most efficacious, followed by hydroxy apatite, known as a peptide adsorber. The most widely used antiperspirant ingredient, aluminum chlorhydrate, was superior compared to talc, which showed almost no effect at all, but was significantly ineffective in comparison with zinc oxide. The quenching mechanism of zinc oxide can be estimated as shown below:

$$2C_4H_9COOH + ZnO \rightarrow (C_4H_9COO)_2Zn + H_2O$$

CONFIRMATION OF THE QUENCHING MECHANISM BY FT-IR

The FT-IR spectrum of zinc oxide-treated short-chain fatty acid aqueous solution is shown in Figure 5. The strong absorption band observed near 1600 cm^{-1} can be assigned as the carboxylate anion of short-chain fatty acid zinc salt. The absence of an absorption at 1700 cm^{-1}, which should be observed in the presence of free fatty acids, convinced us that the expected reaction as shown below was actually proceeding:

$$2RCOOH + ZnO \rightarrow (RCOO)_2Zn + H_2O \text{ (R: alkyl group)}$$

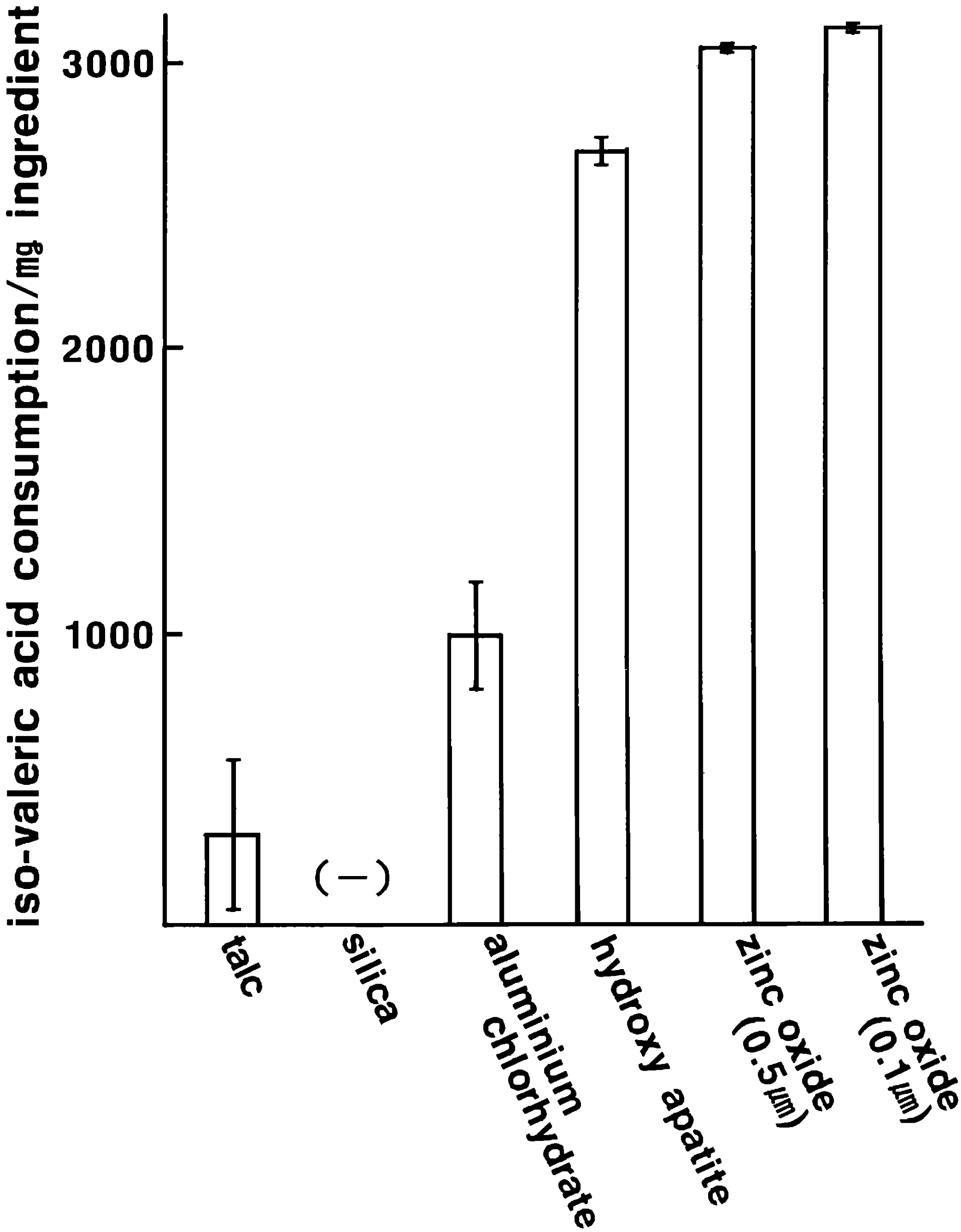

Figure 4. Isovaleric acid consumption values of various ingredients. The larger the value, the greater the efficacy of the ingredient to quench isovaleric acid odor.

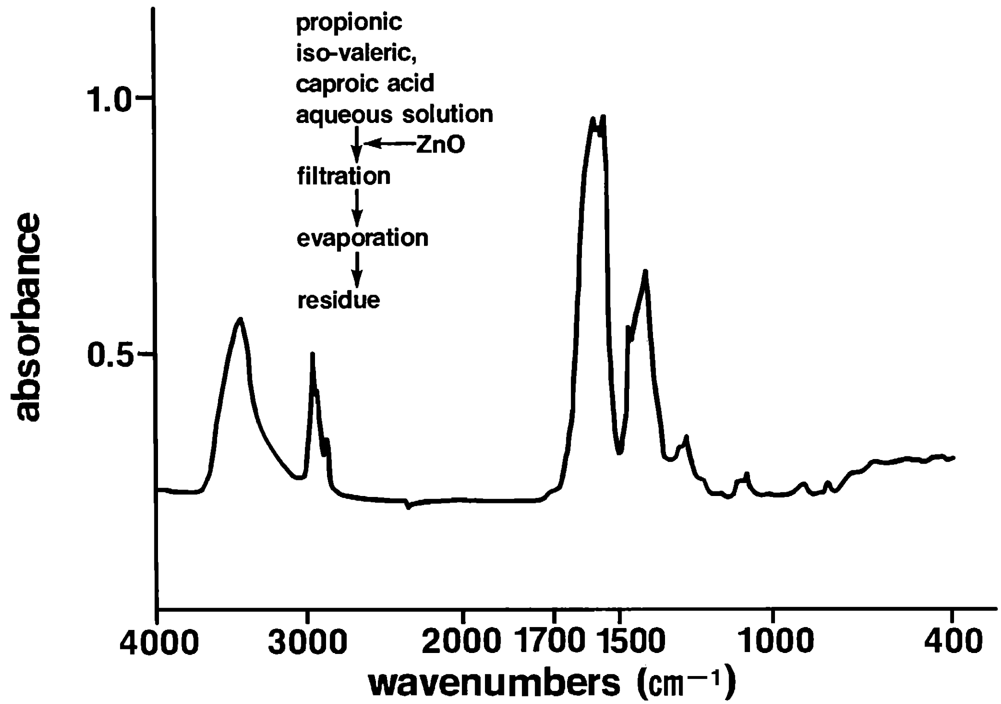

Figure 5. FT-IR spectrum of zinc oxide-treated short-chain fatty acids. The strong absorption band around 1600 cm^{-1} is assigned as the carboxylate anion of short-chain fatty acid zinc salt. The absence of an absorption band at 1700 cm^{-1} shows that no free short-chain fatty acids are present.

FORMATION OF A ZINC OXIDE/NYLON HYBRID POWDER

As can easily be predicted from the microscopic photograph shown in Figure 6, spherical nylon powder has a smooth texture. A photograph of a composite or a hybrid powder of zinc oxide and nylon powder is shown in Figure 7. A uniform layer of zinc oxide is clearly observed around the nylon core powder. Some attractive characteristics of the hybrid powder, in comparison with zinc oxide alone, are summarized below.

1. Increases the surface area of zinc oxide
2. Improves the rough texture of zinc oxide
3. Prevents aggregation of zinc oxide
4. The specific gravity of the hybrid powder is controllable
5. Improves the transparency of zinc oxide

By forming a hybrid powder, the surface area of zinc oxide should increase considerably, and hence it should react faster with short-chain fatty acids. The texture of zinc oxide was improved so much that it was indistinguishable from nylon powder alone. Since zinc oxide is uniformly wrapped around nylon powder, the particle size of the hybrid powder should be almost identical with that of nylon powder. This should prevent the clogging of aerosols considerably. As mentioned above, the specific gravity of the hybrid powder can be controlled by changing the amount of zinc oxide to be coated on top of the nylon powder. The optimum amount to form a single layer was found to be

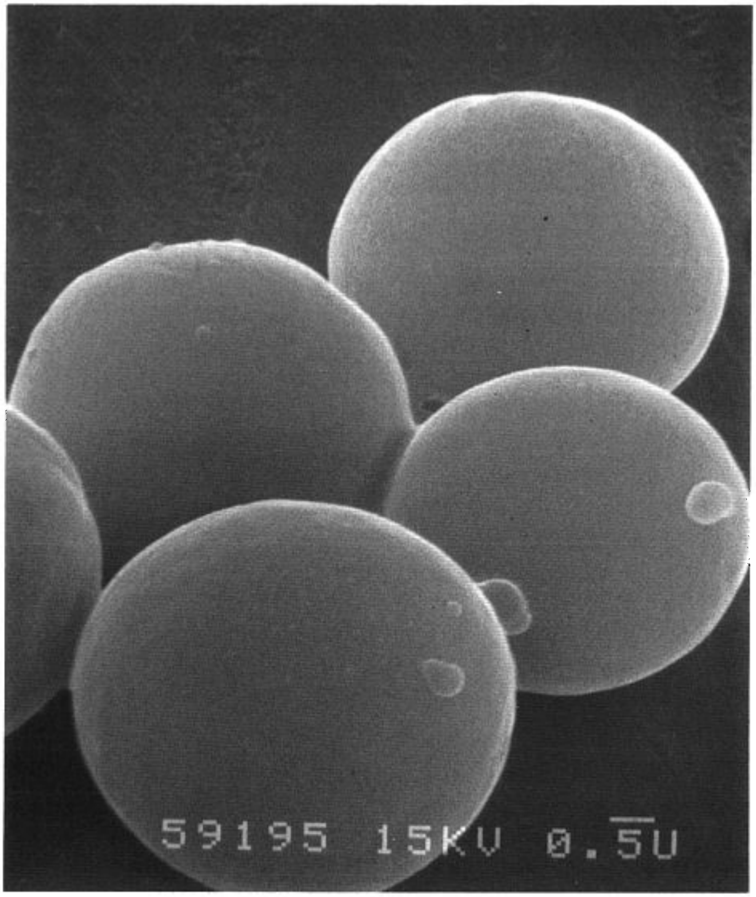

Figure 6. Photomicrograph of spherical nylon powder. The smoothness of the surface is readily observed.

around 20%. Amounts above 20% would overload the nylon surface, which consequently would result in rough texture, and amounts below 20% would leave some portions of the surface naked. When applied to the skin, the hybrid powder was more transparent than zinc oxide alone.

EFFICACY OF QUENCHERS FORMULATED WITH HYBRID POWDER ON FOOT ODOR

Odor assessment results of formulae 1 and 4 are shown in Figure 8 and Figure 9, respectively. The horizontal axis is taken as the time in hours after the first application. The vertical axis is taken as the mean foot odor intensity self-evaluated by the subjects. Out of the four formulae, formula 1 was the most efficacious, due to the high content of zinc oxide, but its texture was the worst, and several aerosols were clogged by it. The efficacy of formula 4, i.e., a conventional formula with no zinc oxide, was the lowest. Formula 2, containing 30% of hybrid powder, was comparable in efficacy to formula 1 but with a better texture. Formula 3 was found to be more effective than formula 4 but

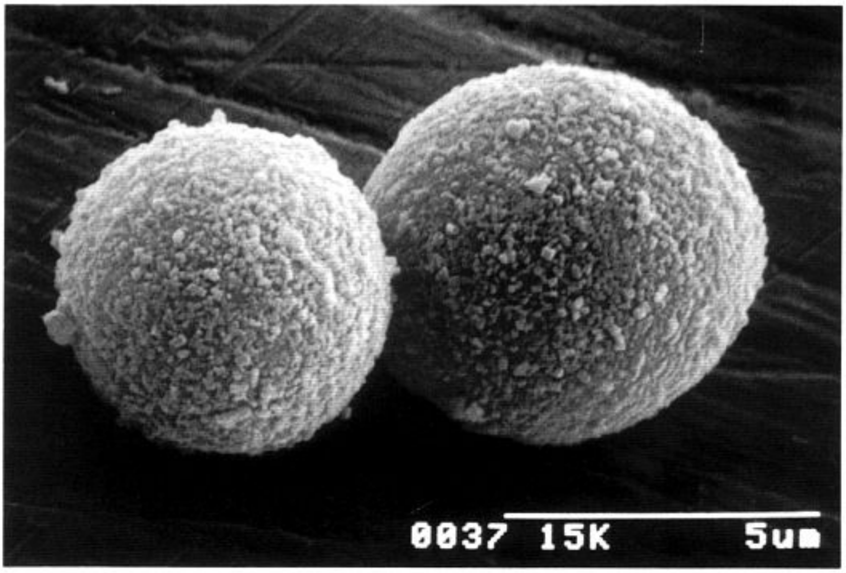

Figure 7. Photomicrograph of hybrid powder. A uniform layer of zinc oxide on the surface of nylon powder is observed.

not as much as formula 2, due to the amount of hybrid powder. No aerosol clogging was reported for formulae 2, 3, and 4. Consequently, the formula of choice is formula 2.

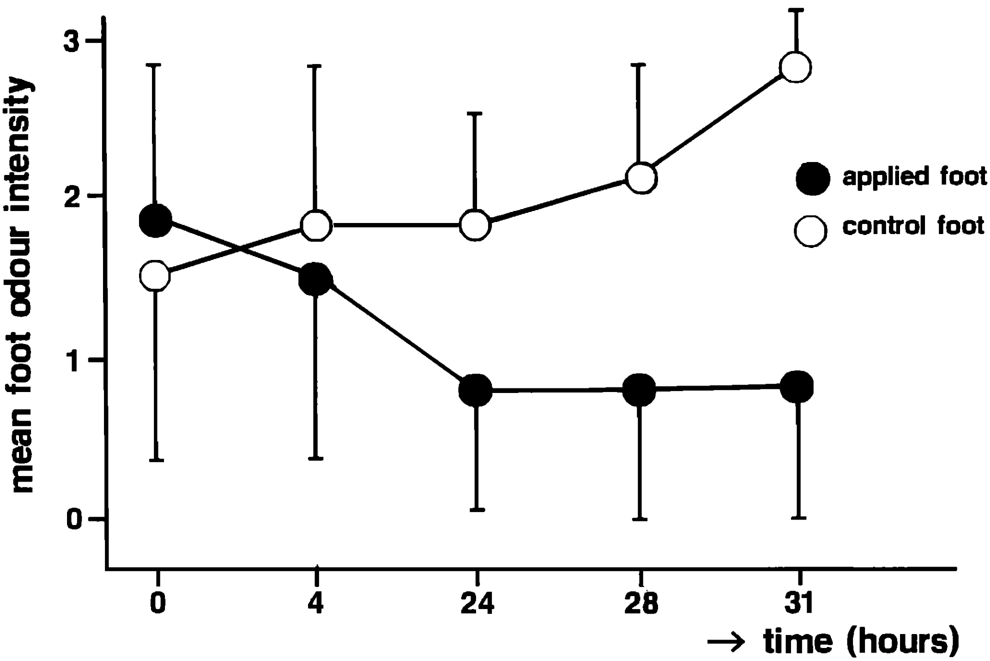

Figure 8. Odor assessment result of formula 1 on foot odor. Foot odor of the applied foot is suppressed in comparison with that of the control foot.

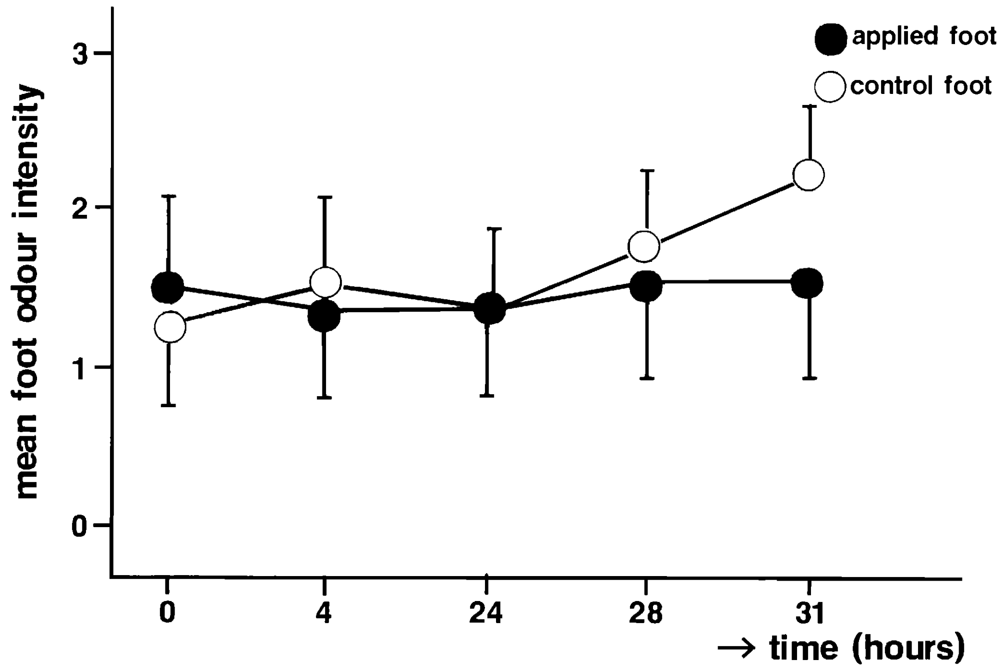

Figure 9. Odor assessment result of formula 4 on foot odor. Foot odor of the applied foot is only slightly suppressed in comparison with that of the control foot.

EFFICACY OF QUENCHERS FORMULATED WITH HYBRID POWDER ON AXILLARY ODOR

The results of the double-blind trials are shown in Table II. The total number of subjects was 18, since two subjects resigned during the assessment. Hybrid powder containing quencher A showed a statistically significant deodorant effect over quencher B, a conventional formula. Hybrid powder-formulated quenchers were proven to be efficacious not only on foot odor but also on axillary odor.

CONCLUSIONS

Short-chain fatty acids have been identified not only in the foot and the axilla but also in other sites of the human body such as the vagina (3), hair and scalp (4), and physio-

Table II
Double-Blind Assessment Results of Quenchers A and B

Comparison of efficacy	Evaluation
$A \gg B$	4
$A > B$	8
$A = B$	1
$A < B$	4
$A \ll B$	1
Total	18

Wilcoxon sign-rank test evaluation: $U_0 = 1.7328$; $P_0 = 0.0831 +$.

logical fluids (5). Along with low-molecular-weight compounds containing nitrogen and sulfur, short-chain fatty acids seem to comprise a considerable portion of human body malodors.

The best method to efficiently eliminate short-chain fatty acids was considered to be through chemical reaction converting them into their corresponding odorless metallic salts. Out of the several chosen candidates, zinc oxide was found to be most suitable. Taking into account the several shortcomings that zinc oxide possesses, we have developed a hybrid powder consisting of a spherical nylon resin as the core whose surface is uniformly covered with fine particles of zinc oxide. This hybrid powder overcomes zinc oxide's drawbacks, especially those encountered upon formulating it into deodorant products, without sacrificing any of its deodorizing power. The body odor quenchers formulated with hybrid powder were assessed on subjects with strong foot and axillary odor, and were found to be more efficacious in eliminating malodors as compared with conventional antiperspirants and deodorants.

The hybrid powder body odor quencher is a novel deodorizer that theoretically not only prevents the generation of body malodor as conventional products do, but also chemically "quenches" body malodor once formed from short-chain fatty acids. This concept is applicable to body odors from regions other than the foot and axilla, provided that the key odor components are short-chain fatty acids.

REFERENCES

(1) F. Kanda, E. Yagi, M. Fukuda, K. Nakajima, T. Ohta, O. Nakata, and Y. Fujiyama, Elucidating body malodour to develop a novel body odour quencher, *15th IFSCC International Congress* Preprints, Vol. 3, 529–562 (1988).

(2) H. Boelens, H. G. Haring, and D. de Rijke, Threshold values of and human preferences for 4-ethyl octanoic and 3-methyl butanoic acid, *Perfum. Flav.*, **8**, 71–74 (1983).

(3) G. Preti and G. R. Huggins: Cyclical changes in volatile acidic metabolites of human vaginal secretions and their relation to ovulation, *J. Chem. Ecol.*, 1, 361 (1975).

(4) N. Goetz, G. Kaba, D. Good, G. Hussler, and P. Bore, Detection and identification of volatile compounds evolved from hair and scalp using headspace gas chromatography, *J. Soc. Cosmet. Chem.*, 39, 1–13 (1988).

(5) T. L. Perry, S. Hansen, S. Diamond, B. Bullis, C. Mok, and S. B. Melacon, Volatile fatty acids in normal human physiological fluids, *Clin. Chim. Acta,* 29, 369–374 (1970).