Mechanism and regulation of body malodor generation (2)

-Development of a novel deodorant powder and application as an antiperspirant-

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SUMMARY

We have developed a high performance powder, which has a quenching efficacy not only for short-chain fatty acids and amines, but also for vinyl ketones (1-octen-3-one, cis-1,5-octadien-3-one), newly found as other key compounds in axillary malodor. By investigating various powders known to have a quenching efficacy, we finally developed a highly porous silica bead containing magnesium oxide.

We found that the superior deodorant effect performed by this powder was the result of multiple effects due to both an excellent physical adsorption capability from its high porosity and a specific adsorption of vinyl ketones by magnesium in the powder.

An antiperspirant formulation containing both this powder and a *Morus alba* extract showed good efficacy as a deodorant.

INTRODUCTION

Body malodor is the unpleasant odor generated by a microbial metabolism from the secretions of the eccrine gland, apocrine gland and sebaceous gland. In previous studies, short-chain (C5-C11) fatty acids, amines, and steroids were detected from body malodor [1][2].

We have newly identified vinyl ketones (1-octen-3-one, cis-1,5-octadien-3-one) in body odor and found that these ketones are additional key compounds causing axillary malodor, and the generating mechanism is estimated to be the oxidation of the unsaturated fatty acids catalyzed by the iron ion [3].

On the other hand, various materials are used in antiperspirant formulations in order to reduce body malodor. Many conventional antiperspirant formulations are designed to inhibit the generation of body malodor using antiperspirant agents and antimicrobials. Moreover, recent antiperspirant formulations include not only the compounds that inhibit the generation of body malodor but also that quench the generated body malodor, e.g. powders. However, all of these antiperspirant formulations are aimed to quench short-chain fatty acids and/or amines that are generated by the microbial metabolism, and not to quench the vinyl ketones.

In the preceding chapter in this book, a *Morus alba* extract was found to repress the generation of vinyl ketones due to its remarkable antioxidizing effect.

Therefore, we developed a high performance powder, which has the quenching efficacy not only for short-chain fatty acids and amines, but also for vinyl ketones, and examined its application to antiperspirant formulations.

METHODS

Headspace GC analysis for evaluation of the quenching efficacy

A 100 mg of various powders were measured by weight, and put into a vial for the GC analysis, and then added 30μL of the malodor compound solution (the concentration is shown in Table 1) . The vial was then closed and placed in a water bath for 5 minutes at 34℃. The one mL headspace gas in the vial was determined for the concentration of the malodor compound using Headspace GC (the conditions are shown in Table 1).

The quenching efficacy of each powder was calculated as follows using the ratio of the peak area with or without the powder.

The malodor compounds were as follows: iso-valeric acid (IVA) as a representative of a short-chain fatty acid, trimethylamine (TMA) as a representative of an amine, and 1-octen-3-one (OEO) as a representative of the vinyl ketones.

Rate of quenching(%) = (1 − peak area with powder / peak area without powder) x 100

Table-1 Experimental condition for Gas Chromatography

Compound	iso-valeric acid (IVA)	trimethylamine (TMA)	1-octen-3-one (OEO)
Compound concentration	2% aqueous solution	0.5% aqueous solution	0.5% aqueous /Ethanol solution
Detector	FID	FID	FID
Column	Agilent HP-INNOWax 0.25mm i.dx30m df=0.25μm	Chrompack Pora PLOT Q 0.32mm i.dx25m df=10μm	Agilent HP-INNOWax 0.25mm i.dx30m df=0.25μm
Column temperature	100℃→160℃	180℃	80℃→130℃
Temperature condition	5℃/min ascending	isothermal	5℃/min ascending
Injector temperature	180℃	180℃	180℃

Powder surface analysis using Atomic Force Microscope (AFM)

The scanning probe microscopy Dimension 3100 (Digital Instruments) was used for the analysis. The sample was fixed to the table using adhesives and measured in the tapping mode. D-NCH (silicon, Nanosensors) was used as the chip.

Electron Spectroscopy for Chemical Analysis (ESCA)

A 500 μL sample of OEO was added to a vial, and the filter paper that carried the 300 mg of powder was placed in the vial without touching the OEO. The vial stood at room temperature for 24 hours.

The atomic concentration and chemical bonding structure of the powder treated with or without OEO were analyzed by ESCA. The ESCA analysis was performed using Quantam 2000 (ULVAC) with Alα as the X ray source. Energy proofreading used C1s (284.6eV).

Evaluation of deodorizing efficacy

Twenty-seven male subjects who have body odor were selected for testing. These subjects wore shirts of which odorless gauze was sewn on the portion of the axilla after washing their body with a non-fragrance soap on the evening prior to the examination. Two spray-type antiperspirant formulations were applied on each axilla on the morning of the examination day, and shirts were collected at night. The trained evaluators evaluated the intensity of the axillary malodor of the shirt using the following five steps (relative score).

+2 ; efficacy of A > efficacy of B

+1 ; efficacy of A . efficacy of B

0 ; efficacy of A = efficacy of B

-1 ; efficacy of A . efficacy of B

+2 ; efficacy of A < efficacy of B

Formulation A: contained aluminum chlorohydrate, HP-MS Powder, *Morus alba* extract

Formulation B: contained aluminum chlorohydrate, MS Powder

RESULTS AND DISCUSSION

Quenching efficacy of various powder

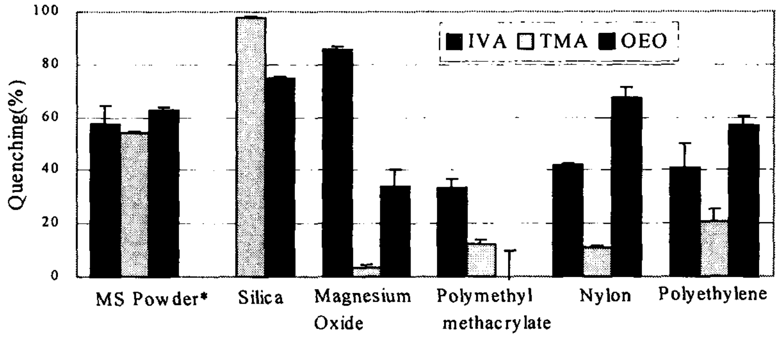
We evaluated the quenching efficacy of the various inorganic/organic powders available as cosmetics using the headspace GC (Fig. 1).

Magnesium oxide (Magnesia) and silica showed a high quenching efficacy for IVA and TMA, respectively. The quenching mechanism of magnesia is presumed to be a chemical interaction between IVA and magnesia to convert them into nonvolatile short-chain fatty acid salts. On the other hand, that of silica is presumed to be hydrogen bonding between the hydroxy group on the surface of the silica and TMA.

As the magnesia/silica (a silica bead containing magnesia, named MS powder), which has both these advantages, had a certain quenching efficacy level not only for IVA and TMA, but also OEO. A previous study has shown that the quenching mechanism of the MS powder is both a chemical adsorption and a physical adsorption capability due to its porosity [4]. Therefore, we estimated that OEO was quenched by the MS powder due to its physical adsorption because the vinyl ketone has little ionicity.

Various silicas, which have different specific surface areas, were evaluated for quenching efficacy. The result shows a strong correlation between the specific surface area and quenching efficacy (Fig.-2).

Therefore, we postulated that the quenching efficacy might be improved by preparing a highly porous MS powder.



*magnesium oxide-silica complex powder

Fig.-1 Quenching efficacy of various powder.

Data means the average and SD of three experiments.

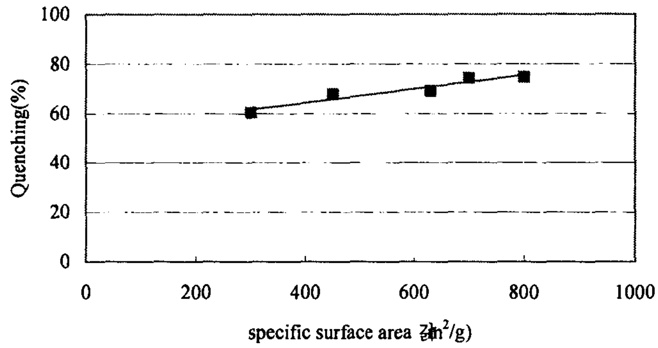


Fig.-2 Relationship between specific surface area and quenching efficacy (OEO) of silica.

Preparing high porous MS powder

In order to obtain a highly porous MS powder, we used the process shown in Fig.-3.

The newly prepared powder, named HP-MS powder, was confirmed that it was more porous than the MS powder in the view of its physical properties and the atomic force microscope (AFM) photograph (Fig.-4).

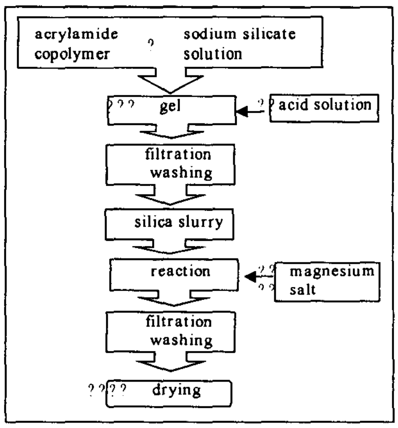


Fig.-3 Manufacturing process of HP-MS powder.

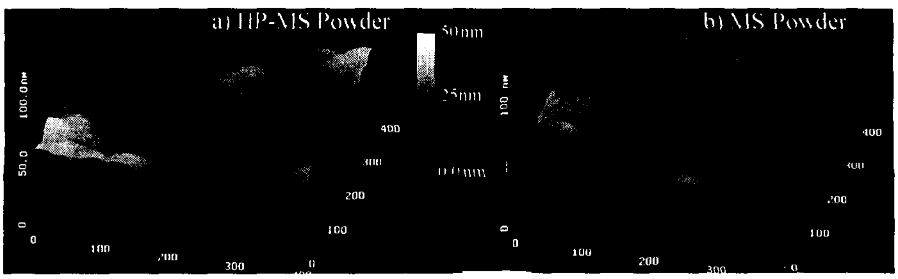


Fig.-4 AFM Image of HP-MS Powder(a), MS Powder(b).

Quenching efficacy of HP-MS powder

As compared to the MS powder, the quenching efficacy of the HP-MS powder for OEO improved as expected, and furthermore, its rate of quenching also improved for IVA and TMA (Fig.-5). The effect of the increasing porosity on the quenching efficacy has been confirmed.

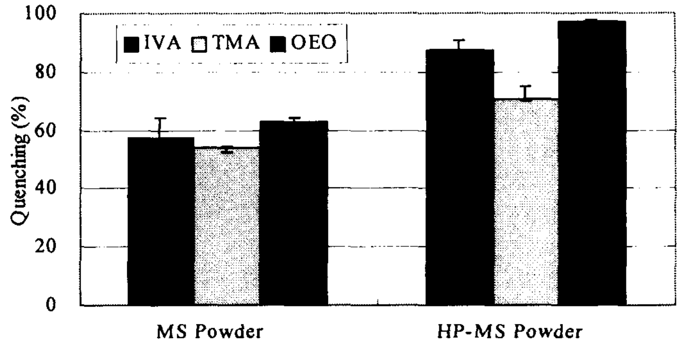


Fig.-5 Quenching efficacy of MS powder and HP-MS powder.
Data means the average and SD of three experiments.

The quenching mechanism of HP-MS powder for OEO

We postulated that the quenching efficacy for OEO would be optimized by increasing the amount of adsorption in the pores.

However, even when the specific surface areas are almost equal, the rate of quenching of the HP-MS powder is higher than silica (Fig.-6). We thought that there is another quenching mechanism other than the porosity. We then postulated that the OEO adsorption capacity of magnesia was higher than silica.

In order to verify this hypothesis, the C1s peak shift and atomic concentration of the surface of the OEO-treated powder was analyzed by ESCA. As shown in Fig.-7, when the carbon ratios of the untreated silica and OEO-treated silica were compared, there was little change in the ratio. On the other hand, the carbon ratio of the OEO-treated magnesia was higher than that of the untreated magnesia.

Furthermore, the C1s spectrum was analyzed in detail. The shoulder peak near 287eV that belongs to the carbonyl group of ketones was not detected on the OEO-treated silica (Fig-8b). On the contrary, this peak was detected on the OEO-treated magnesia (Fig-8a). These results showed that OEO was specifically adsorbed by the magnesia.

With these results, the quenching mechanism of the HP-MS powder for OEO was both its excellent physical adsorption capability due to its high porosity and a specific adsorption of vinyl ketones on the magnesium molecule in the powder.

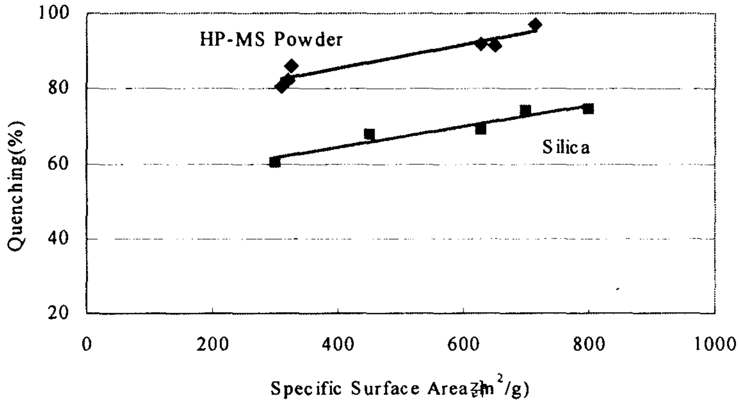


Fig.-6 Relationship between specific surface area and quenching efficacy of two kinds of powders.

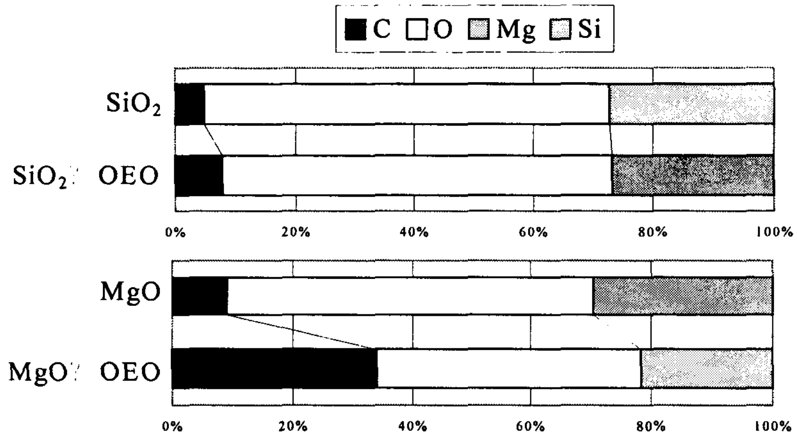


Fig.-7 Surface atomic concentration on silica and magnesium oxide treated with / without OEO.

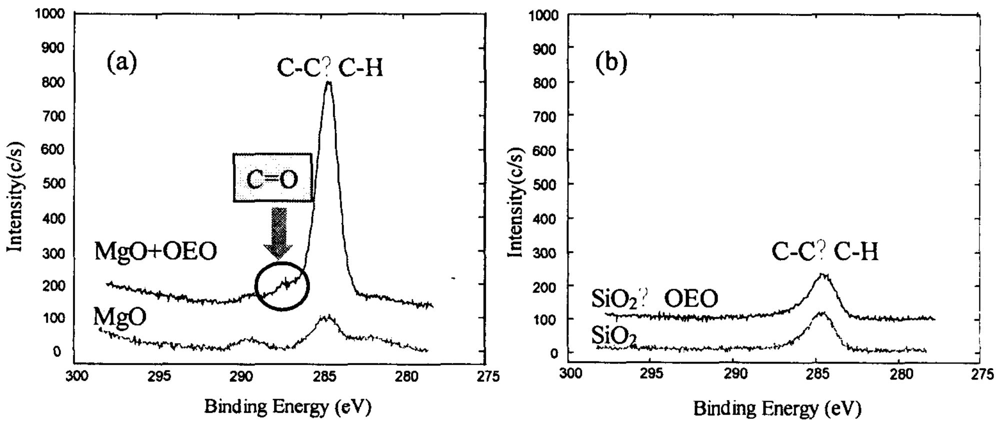


Fig.-8 ESCA C1s spectra of magnesium oxide (a) and silica (b) treated with / without OEO.

Deodorizing effect in antiperspirant formula

The deodorizing effect for body malodor on the formula of spray-type antiperspirant containing the HP-MS powder and a *Morus alba* extract, which represses the generation of vinyl ketones, was evaluated. As a result of evaluating the odor intensity after using the antiperspirant, the efficacy percentage that formulation A (contained the HP-MS powder and a *Morus alba* extract) was more effective than formulation B (contained the MS powder), was 67%. The efficacy that percentage formulation B was more effective than formulation A, was 22%.

CONCLUSION

We searched for a powder, which has the quenching efficacy not only for the short-chain fatty acids and amines, but also for vinyl ketones, and developed the high porous magnesia silica (HP-MS powder).
From the analytical results using GC and ESCA, the quenching mechanism of the HP-MS powder for vinyl ketones was demonstrated that it has both an excellent physical adsorption capability due to its

high porosity and a specific adsorption of vinyl ketones on the magnesium in the powder.
An atiperspirant formulation containing both the powder and *a Morus alba* extract showed good efficacy as a deodorant.

REFERENCE

[1] X.Zeng, J.J.Leyden, H.J.Lawley, K.Sawano, I.Nohara G.Preti, *J. Chem. Ecol.*, **17(7)**, 1469-1492(1991)

[2] X.Zeng, J.J.Leyden, J.G.Grand, A.I.Spielman, K.J.Mcginley, G.Preti, *J. Chem. Ecol.*, **18(7)**, 1039-1055(1992)

[3] N.Ichinose, S.Iida, T.Gomi, K.Someya, K.Hirano, M.Ogura, S.Yamazaki, K.Sakurai, "Mechanism and regulation of body malodor generation (1)" in this book

[4] A.Sambe, T.Kuwayama, H.Takenaka, S.Yoshimune, K.Ishida, *J.Soc.Cosmet.Chem. Japan.*, **29**, 55-63(1995)