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A STUDY ON THE DEVELOPMENT AND THE DEODORIZING CAPABILITY OF METAL-PHTHALOCYANINE PROCESSED STUMP SOCKS FOR AMPUTEES

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KEY WORDS

Metal-Phthalocyanine derivative; artificial enzyme; Kobe Stump Socks; deodorant effect; amputee

ABSTRACT

The socks which were treated with Metal-Phthalocyanine, a derivative of an artificial enzyme, were developed by the author and called Kobe Stump Socks(KSS). KSS was made of a cotton cloth that had undergone an ammonium salt cationization process and also a Metal-Phthalocyanine process. The study from a bacteriological view and the moisture absorption effect of KSS revealed that the mechanism of the deodorizing ability was bared on the decomposition function of Metal-Phthalocyanine, while the antibacterial function came from the cationization and also that the high water absorption speed and capacity further enhanced these two functions.

In this report, the author studied the deodorizing capability of KSS. To measure the adherence of an odor substance, ammonia, a testing device that measured this adherence was used. As a result, the adherence of ammonia to KSS was more than three times that of an unprocessed cloth.

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KSS had been used as stump socks on the stumps of amputees who were using prosthetic limbs, and a snuff test on the difference of the odor strength inside the socket was done. Of 33 subjects, 32 recognized a deodorizing effect. From these facts, KSS was proven to dry and deodorize the limb surface with the moisture absorption effect and deodorizing capabilities due to the Metal-Phthalocyanine process. These characteristics were never recognized in other stump socks. These date mentioned above suggested that KSS was the best material to deodorize prosthetic limb sockets.

INTRODUCTION

In our country, Japan, the hot and damp conditions of summer are uncomfortable problems for the users of prosthesis. It can also cause bad odors and stump eczema which sometimes makes it impossible to use a prosthesis.

Though the odor problem in the socket is well known among the clinicians and the users of prosthesis, no study concerning to the odor problem can be found. This would be due to the difficulty of analyzing the subtle odor, and also to the fact that the amputees give up on the odor problem because of their low emphasis on quality of life(QOL), or the pursuit of their own comfort.

The author has tried to improve the QOL and comfort of the amputees by working on the odor from the stump socket. In trying to find a simple, yet long lasting method of deodorization by using scented sprays or perforated sockets, the author tried to apply the process that Shirai et al.[18,19,20,21] developed for deodorizing bedclothes. The stump socks which were processed with a Metal-Phthalocyanine derivative; an artificial enzyme, used and placed directly on the skin of the amputee. With the cooperation of Shirai and a manufacturer, a deodorizing, antibacterial stump sock was successfully developed and called Kobe Stump Socks (KSS).[5] The conventional stump sock is made of unprocessed pure cotton cloth. The material used to make KSS was obtained by applying succeedingly an ammonium salt cationization process and a Metal-Phthalocyanine process to the cotton cloth.

The untoxicity of KSS was already proven by an independent organization through acute toxicology and skin patch tests.

The previous experiment[4] revealed that KSS kept absorbing water at a consistent rate immediately after the immersed in water. Though cationization was related to the absorption ability, Metal-Phthalocyanine processing further enhanced the speed.[4,6] According to the bacteriological studies,[22,23] the number of staphylococcus epidermis was reduced to less than 1/10, and the number of E.coli was reduced to about one half with in 4 hours, respectively. No significant change was seen for staphylococcus aureus. As for the degree of cationization and Metal-Phthalocyanine, the higher the concentration of the cationizing agent, the higher the antibacterial function was observed. No antibacterial function was mostly observed for Metal-Phthalocyanine cloths. Therefore, the mechanism of deodorizing and antibacterial function of KSS could be explained as following : the deodorization is due to the decomposition function of Metal-Phthalocyanine and the antibacterial function is due to cationization. Furthermore, the high speed water absorption ability would further enhance these effects.[4,5,22]

According to Kamitani et al.,[13] KSS trapped and killed 90% of the bacteria on contact because of the cationization and Metal-Phthalocyanine process. This would keep the wound sanitary and help the recovery.[13] This also suggested that unlike the former conventional covering materials that contained antibacterial substances, the bacteria suppressing function of KSS was fared not an gradual release of antibacterial substances but on trapping and killing bacteria by the cationization. These combined functions of KSS would play a part of the absorption and decomposition of organic material, and even the removal of necrosis tissue and pus. Based on the previous KSS studies, the author measured the deodorizing effect of KSS by an adherence test of an odor substance after applying KSS on the stump of the amputees who used prostheses.

MATERIALS AND METHODS

1.Materials

A.Kobe Stump Socks(KSS) were cut into 10cm x 10cm pieces .

B.Pure cotton cloth(unprocessed cloth) was used as a control.It had been treated with neither cationization nor the Metal-Phthalocyanine processes. It was cut into 10cm x 10cm pieces as well.

C.For the deodorization test with stump socks worn by amputees, stump socks that matched the actual stumps were manufactured with KSS and were worn in place of the former conventional the stump socks(Figure 1).

2.Methods

1)Measurement of the deodorizing ability of Metal-Phthalocyanine processed stump socks (KSS)

Adherence of ammonia gas molecules onto KSS was measured by using a quantitative adherence analysis device (Figure 2). Ammonia was used as the model gas, and its adherence was measured at room temperature(21℃). This vacuum machine used both an oil diffusion pump and an oil per rotatory pump under constant volume. The vacuum achieved was at least 10^{-4}mmHg. Approximately 2g of either the KSS or the control cloth(the unprocessed cloth (10cm x 10cm)), was put and measured in the device's sample tube. In order to remove the water and other substances that might adhered prior to the test, samples were preprocessed with approximately one hour of a vacuum exhaust system at 90℃. After returning to room temperature, the fixed amount of ammonia was introduced. Ammonia pressure at an adherence equilibrium 0.1×10^{-1} -1.0×10^{1}mmHg was measured by a ULVAC capacitance manometer to obtain the adherence amount per 1g of sample. Until ammonia equilibrium pressure of about 5.3 mmHg was achieved, each of the four KSS samples and one control sample were measured.

2) Deodorization of the stump socket with prosthesis

Participants in the study, were thirty-three amputees hospitalized at Hyogo Rehabilitation Center. 30 male and 3 female. They ranged from 6 to 76 in age, with the average ages of 34.87±3.14. As for the site of amputation on the subjects, 21 were transtibial, 2 were transfemoral, 5 were Syme, 2 were transhumeral, and 3 were transradial.

Three occupational therapists evaluated the odor strength of the stump sockets. They had been trained for the odor strength a snuff test

according to the six-level odor description method (Table I) of the Ministry of Labour's National Institute of Health Sciences.

Each amputee entered the 27-31℃ training room at a predetermined time. They removed the prosthetic limb with wearing a regular stump sock. Using the six-level method, the three occupational therapists immediately evaluated the odor of the stump socket. The odor strength was determined by the level agreed upon by all three evaluators. This evaluation was termed the pre-application odor. Then, a KSS stump sock was applied to the stump and the prosthetic limb was put back on, and the amputee spent 24-hours using the prosthesis as usual. The same period of time per day was applied to both the KSS stump sock and a regular stump sock. After the 24-hour period, at the same time of the day, the odor strength was evaluated again. This process was repeated until the odor strength reached 0 - 1. This evaluation was termed the post-application odor. After the odor level reached 0 - 1, follow-up evaluation was performed once a week to see if the odor level could be maintained. Pre- and post-application evaluations were compared for each case, and the results were tested with Wilcoxon's signed rank test.

For transtibial cases, the relationship between the length of time of prosthetic leg use per day and odor strength were tested. The relationships between age and odor strength were also tested.

RESULTS

1.Measurement of the deodorizing ability of Metal-Phthalocyanine processed stump socks (KSS)

By testing for the adherence amount at equilibrium at room temperature(21℃) as shown in Figure 3, the amount of time required to reach equilibrium was from minutes up to approximately two hours, depending on the pressure. The adherence amount for KSS samples was a little over three times that of the control samples(Figure 3). Among the KSS samples, all four materials showed similar results.

2.Deodorization of the stump socket with prosthesis

For all cases, the odor strength before KSS application and the odor

Figure 1. Kobe Stump Socks (KSS) have been worn.

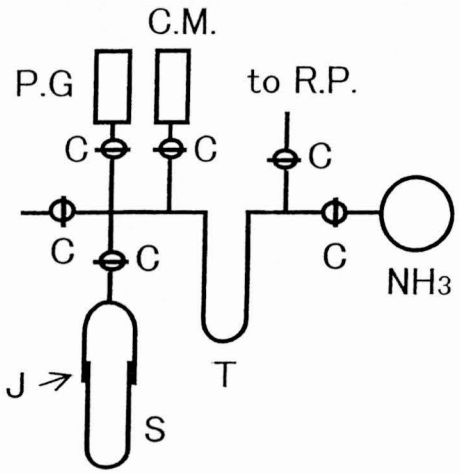


Figure 2. An Ammonia Adherence Testing Device.
S : a material tube
J : connection
P.G : vacuum (Okano Works PG-25)
C.M : a capacitance manometer (ULVAC GM-1000)
T : tortuous U pipe.
R.P : oil rotary pump
NH3 : An ammonia
C : a valve

Table I. The six-level odor description method of the Ministry of Labour's National Institute of Health Sciences.

criteria
0 - no smell
1 - little smell
2 - weak but recognizable smell
3 - easily recognizable smell
4 - strong smell
5 - severe smell

strength after five days of application are shown in Figure 4. Except for one case, the deodorizing effects were observed. Wilcoxon's test demonstrated a significance of $p<0.0001$. Of the 33 cases, 11 cases reached the odor level of 0 -1 by third day, and 19 cases reached the odor level of 0 - 1 by the fifth day. On the fifth day, 2 cases had an odor level of 2, and a case had an odor level of 3. By further examination of 21 transtibial cases, for 4 cases making the use of the prosthetic leg 10 hours or less per day, the odor level before and after use were not significantly different ($p =0.0656$) (Figure 5). However, for 17 cases by which prostheses were used for 10 hours or more everyday, the odor strength before and after use had a significant difference of $p=0.0002$ (Figure 6). For the transtibial amputees below the age of 40, the deodorizing effect was significant at $p=0.0046$. Also, when the pre- and post-application odor levels for the transtibial amputees of age 40 and above were compared, the deodorization effect was significant at $p=0.0042$ (Figure 7). Therefore, KSS demonstrated it's deodorizing ability significant by comparing pre- and post-application odor levels, independent of the age of the amputees.

DISCUSSION

The odor from the socket of a prosthesis is a serious problem for an amputee and the medical workers. Generally, there are three methods to fight odor. One is sensory deodorization, meaning to mask the odor with a stronger smell(s). The second is physical deodorization, where odor-causing molecules are trapped in a porous material to prevent volatilization. The last is biological deodorization, where decomposition of the odor causing molecules with enzymes which are produced by micro organisms.[16)]

Because of the characteristics and adaptability of plastic materials and the longevity of the effect, these three methods were not very promising, and there was requested other alternative deodorization method.[10)] According to Shirai,[19)]"odor" is the volatile compound which macromolecules are produced mainly from the bacterial decomposition of protein, carbohydrates and high quality fatty acids. So far 300-400 odor-

causing substances have been identified. Among them, the especially harsher substances include hydrogen sulfide, mercaptan, acetaldehyde, ammonia, amine, indole and scatol.

In 1980, Shirai developed a type of fabric that used the artificial enzyme derivative, Metal-Phthalocyanine to apply the biomimetic effects to decompose odor-causing molecules in an enzyme-like catalytic manner. This fabric oxidized and decomposed aldehyde, hydrogen sulfide, mercaptan, phenol, indole and scatol.[20] The characteristics of this fabric were: 1) It eliminated odor by oxidizing the odor-causing molecules with molecular oxygen into a different substance. 2) The amount of substance in the atmosphere was very low compared to the amount of catalyst, so the reaction completed almost 100%. 3) The reaction was an enzyme-like cyclic reaction, so it lasted longer than other chemical reactions. 4) Reaction was fairly quick. 5) Water did not interfere with the reaction. 6) Compared to enzymes, there were less environmental constraints such as pH and temperature and it was also less expensive. 7) It was easy to use and flexible enough to be manufactured in various shapes, so a wide area of application was possible. These characteristics suggested this material would be an ideal candidate for deodorizing the prosthetic socket.

In 1986, with developing a deodorizing antibacterial fabric, Shirai's Metal-Phthalocyanine derivative was able to apply directly on the skin. Since then, the deodorizing effect on prosthetic limb users and the effect on the improvement of stump eczema and the mechanism of these effects had been studied by the author.[5] Initially, the application of the Metal-Phthalocyanine derivative on the stump socket plastic itself or the application of the deodorizing fabric on the inside of the socket was attempted. However, these ideas were discarded due to the characteristics of the plastic and socket adaptability.[10] Then the approach of deodorizing the socket by producing a socket sock with the deodorizing fabric was tried. This sock could cover the stump of an amputee and be inserted into the socket and called KSS.[5]

The advantages of using KSS for a stump sock were; 1) the ease of use and the absorption of sweat which contributed to the drying of the stump, 2) the amputee had been wearing a sock since the manufacturing days of the prosthetic limb, so the amputee was accepted to it, 3) KSS

had a large surface area and had an improved deodorizing power because it absorbed water, which was the purpose and the characteristics of a stump sock, 4) KSS was inexpensive. Two or three stump socks could be used in an alternating fashion, 5) KSS was also suitable for deodorizing the odor caused by pus from the stump eczema.

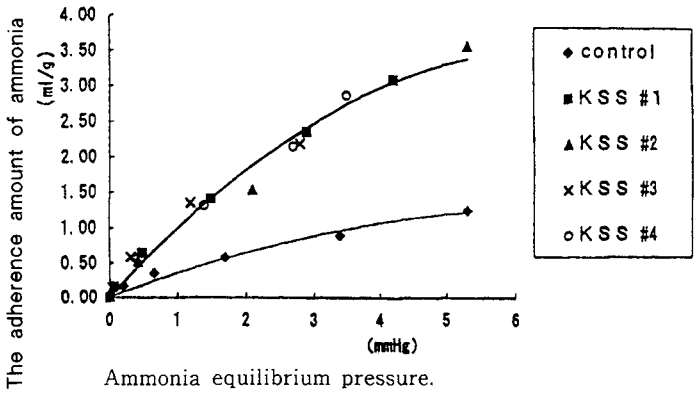
Before the clinical use of KSS, toxicity checks were performed by an independent institute. To prove the non-toxicity of KSS on the skin, patch tests were performed and animal testing was done for acute toxicology of ammonium salt and Metal-Phthalocyanine.[5)]

Initially, for deodorization testing, a conventional stump sock was applied directly to the stump, and KSS was applied over it. After checking for a rash and inflammation on the skin, KSS was applied directly on the stump.[5)]

Usually, the methods used to fight the sweat odor from a prosthetic limb were fenestration of the stump socket, frequent change of the stump sock, the use of a nylon stump sock and the use of powder. Other methods were the use of sweat inhibitors, perfumed sprays, and cleaning of the socket.[5)] Since all of these methods provided only temporary relief, frequent changing of stump socks and spraying were necessary every day. This trouble often led to discontinuing the use of the prosthesis.[5)]

Looking at the past report on the related areas, the research on the inside of the sockets of prosthetic limbs was limited all for the design of sockets.It did not take into account the stress placed on the skin of the stump.[2,3,9,)] Studies on skin deodorization were on tragomaschalia and allergy.[11,12)] Research on the prosthetic limb material studied the durability of these available materials.[17)] No research was found for deodorization of the stump socket itself.

The ammonia adherence testing device proved that the ammonia adherence amount of KSS was three times that of an unprocessed cloth. This suggested that KSS performed its deodorizing function by decomposing most of the trapped odor. From this adherence test, the mechanism of neutralizing ammonia, which was one of the sources of odor from stump eczema of an amputee, was working effectively as was the case in the study by Shirai.[20)] Since the human sense of smell is more effective than any analytic device,[1,24)] the snuff test was chosen. It was



Ammonia equilibrium pressure.

Figure 3. The adherence amount of ammonia.

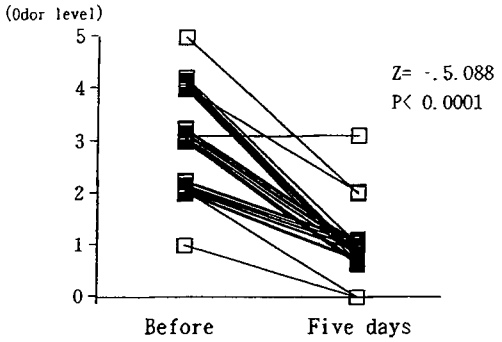


Figure 4. Odor strength in KSS application (33 cases).

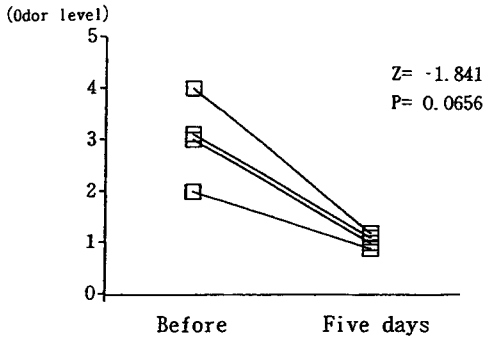


Figure 5. Odor lebel when the length of time of prosthetic leg use per day (10 hours or less).

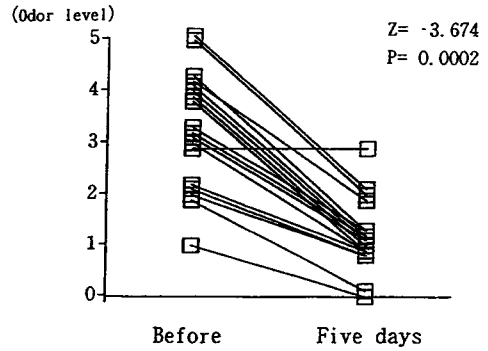


Figure 6. Odor lebel when the length of time of prosthetic leg use per day (10 hours or more).

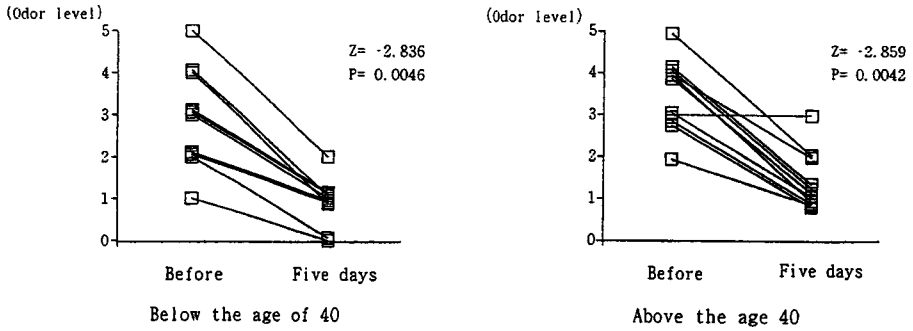


Figure 7. Comparing pre-and post-application odor levels, independent of the age.

also clear from the snuff test that of 33 cases, 32 cases showed improvement of the odor problem with the use of KSS. The study of transtibial prosthesis cases showed that regardless of age of the amputee, longer use of the prosthesis brought better deodorization results with KSS. The higher the deodorization results the longer the use of the prosthesis. This was compatible with the original purpose of a prosthetic limb.

Most of the odor-causing substances were formed by the decomposition of sweat and stratum cutaneus by bacteria.[15)]

Also, in accordance with the high water absorption ability of KSS,[4)] in all cases, the inside of the socket and the stump were dry. This dryness would discourage bacterial growth in the socket.

In conclusion, the mechanism of the deodorization was first, the high water absorption ability, which dried the inside of the socket and stump, and second, the suppression of bacterial growth. KSS also trapped a great number of odor molecules such as ammonia, which would be decomposed by the Metal-Phthalocyanine into harmless substances, thus completed the deodorization in the stump socket of a prosthetic limb.

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