STUDY ON THE INFLUENCE OF POLYOL ON MICROEMULSION GEL SYSTEM

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Microemulsion gel system에 있어서 Polyol의 효과에 관한 연구

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Abstract

This study relates to a microemulsion gel which is applied in various cosmetic preparations because of good appearance, superior stability and a thin, uniform, non-greasy film on the skin.

Main object of this study is to elucidate the influence of polyol(clarifying agent and/or coupling agent in microemulsion) on microemulsion and to establish the optimum conditions for microemulsion gel formation in the view of superior consistency, stability, clarity and pick-up from a container.

The constituents of the system are composed of water, polar ester oil, nonionic surfactant and polyol. Using the three-component phase diagram and the tetrahedral-phase diagram, we have investigated the changes of transparence regions, consistency and resonance effect by an impact in microemulsion gel varying in polyol ratio.

The results of this study showed that the variation in the content of

water and coupling agent has major influence on the microemulsion gel and the optimum formation region of microemulsion gel is the widest when the ratio of glycerine(coupling agent) to water is 63～75%.

It is believed that optimum use of polyol seems to be helpful to obtain the microemulsion gel containing maximum amount of oil phase with minimum amount of surfactant which is recently one of the major problems of cosmetic chemists.

1. Introduction

Unlike normal emulsion, microemulsion gel generally represents transparent appearance and outstanding thermodynamic stability because the particle size of the dispersed droplets is very fine(0.01～0.1μm). Since it forms a thin, uniform and non-greasy film when applied on the skin, microemulsion gel is preferred in various cosmetic preparations.

It is not necessary to do any special mechanic operation such as homogenizing or colloid milling in making. It provides strong appeal of peculiar product to customer with neat and clean image by transparent appearance.

There are two methods in producing this kind of microemulsion gel usually. one is to use ionic surfactant and the other is nonionic surfactant. Since microemulsion gel made by ionic surfactant is not desirable on the point of skin safety, cosmetic chemists have been mostly interested in microemulsion gel by nonionic surfactant which is more mild on skin.

However, microemulsion gel by nonionic surfactant may also irritate the skin because it must contain relatively high surfactant content. Thus, until now, it has not well established in the cosmetic trade on a large

scale.

So, we have intended to develop microemulsion gel containing a desirable large amount of oil with much less surfactant by studying the effect that polyols, which are used in clarity agent or coupling agent of microemulsion gel, have on microemulsion gel system and to develop suitable and diversified product by selecting appropriate ratios of polyol to water.

2. Experimental

2-1. Materials.

To investigate microemulsion gel system made by nonionic surfactant, oil, polyol, and water, we used the following materials. These materials are commercial grade which is not refined.

1) Nonionic Surfactant
   a. Polyoxyethylene(15) Stearyl Ether(Nihon Emulsion; Emalex 615)
   b. " (20) Sorbitan Monooleate(ICI; Tween 80)
   c. " (25) Octyl Dodecyl Ether(Nihon Emulsion; Emalex OD-25 JJ)

2) Oil
   a. Isopropyl Myristate (Inolex; IPM)
   b. Octyl Palmitate (Vandyk; Ceraphyl 368)
   c. Octyl Dodecyl Myristate(Cas Chem; Wickenol 142)
   d. Isostearyl Isostearate (Gattefosse; Isostearyl Isostearate)

3) Polyol

a. Propylene Glycol (Dow Chemical; Propylene Glycol)

b. 3-Methyl-1,3-Butanediol (Kuraray; Isoprene Glycol)

c. 1,3-Butylene Glycol (Daicel; 1,3-Butylene Glycol)

d. Glycerine (Lucky, Korea; Glycerine)

e. Sorbitol (Roquette; Sorbitol)

f. Malbit (Hayashibara; Malbit)

4) Water

Deionized and Distilled Water

2-2. Methods.

1) Sample Preparation

The system of nonionic surfactant/oil/polyol/water was divided into water phase (polyol, water) and oil phase (nonionic surfactant, oil) and then weighed respectively. After water phase and oil phase were heated to 80℃, water phase was slowly poured into oil phase, then it was stirred by a mixing rod and cooled to 40℃.

2) Measurements.

Measurements were done at a constant temperature of 25℃ after 48 hours from sample preparation.

i) Hardness

Hardness was measured by Fudoh Rheometer NRM-2010j-CW using the Adaptor No.3 of 10mmϕ. Hardness over 6 dyne/cm^2 was chosen.

ii) Clarity

Clarity of appearance was visually divided into three stage, "Transparent, Translucent, Opaque".

iii) Pick-up

It is called pick-up when we take some microemulsion gel by finger tip. We observed this status to be divided into good & bad.

iv) Resonance

We observed "resonance" effect, as their own peculiar characteristic, when tapping or gently bouncing on the ware which is contained microemulsion gel.

3) Phase Diagrams

We drew up three-component phase diagrams of the optimum formation regions of microemulsion gel which were evaluated by the above "2) Measurements". In addition, we have made tetrahedral-phase diagram for the regions in three-dimensional form using by Silicon Graphics(CAMAX, Inc.).

3. Results and Discussion

3-1. Results.

According to Mannheim(3), nonionic surfactant should be soluble and form a clear dispersion in the aqueous phase on microemulsion gel system by nonionic surfactant.

Therefore, a moderate hydrophile HLB(Hydrophile Lipophile Balance) is required. In addition, according to Chester(2) and Lower(6), adequate HLB range of nonionic surfactant should be 7-14, 9-15, respectively. So, we

have tested the preliminary experiment using polyoxyethylene(15) stearyl ether(HBL=12), polyoxyethylene(20) sorbitan monooleate(HLB=15), polyoxyethylene(25) octyl dodecyl ether (HLB=14) whose HLB ranges are 12∼15.

As a result, surfactant of branched alkyl chain such as polyoxyethylene(25) octyl dodecyl ether was more effective than surfactant of linear alkyl chain on the formation of microemulsion gel.

As oils, we can generally get satisfactory microemulsion gel, by selecting hydrocarbon oil or ester oil. In this experiment, we selected ester oil because ester oil is more common in current cosmetic formulation for its light and mat feeling. We have carried out the preliminary experiment with four ester oils-isopropyl myristate, octyl palmitate, octyl dodecyl myristate, and isostearyl isostearate. We came to the conclusion that octyl palmitate was more effective to form microemulsion gel.

Based on the above experiments, we have used system of polyoxyethylene(25) octyl dodecyl ether(POE(25) ODE)/octyl palmitate(OP)/polyol/water. Then we have studied the optimum formation regions of microemulsion gel according to the content ratio variation of polyol and the likes. Finally, the three-component phase diagram and the tetrahedral-phase diagram are drawn.

1) Formation region of microemulsion gel without coupling agent.

Formation region of microemulsion gel of the system of POE(25) ODE/OP/Water is drawn on Fig.1.

As you can see Fig.1, the formation region of microemulsion gel leans to POE(25) ODE and water. This indicates that it contains a very little amount of oil(1∼10%), even though a large amount of surfactant(30∼45%) has been used. Also, on this formation region, the hardness shows very

high value(over 100 dyne/cm^2) and the application feeling is not smooth. So, it is very difficult to treat and very limited to apply on products.

2) Formation region of microemulsion gel with coupling agent.

a. Selection of polyol which is coupling agent.

To evaluate which polyol is the most effective to form microemulsion gel, we have tested comparative experiment with several compositions as shown on Table I and we have obtained the following result as shown to Table II.

As you can see Table II, diols formed opaque microemulsion gel on a composition of A which contains a large amount of surfactant and less oil content, whereas polyols which are over triol formed transparent microemulsion gel.

Furthermore, diols did not form microemulsion gel on the composition which contains a large amount of oil and less surfactant content. Among polyols, which are over triol, sorbitol and marbit formed opaque microemulsion gel. But in case of glycerine on all composition experiment, it creates transparent microemulsion gel. It can be assumed that microemulsion gel formation on the composition which has much surfactant content and less oil content is caused by a large amount of surfactant, rather than by effect of polyols and that microemulsion gel formation on the composition which has less surfactant content and much oil content is caused by the effect of polyol, which was used by coupling agent, judging from that microemulsion gel is formed even though the effect of surfactant is getting diminishing. Particularly from this experiment, glycerine is the most effective on microemulsion gel formation among those polyols.

b. Microemulsion gel formation following by ratio variation of water and glycerine.

On the system of POE(25) ODE/OP/Glycerine/Water, we observed the status of microemulsion gel by changing the content ratio of water and glycerine. The change of formation regions is shown in Fig. 2 with the three-component phase diagram. From the Fig. 2 Diagrams, as the content ratio of glycerine to water is getting increasing, the formation region of microemulsion gel tends to the widened and then narrowed. It also shows the formation of microemulsion gel which contains a large amount of oil and a little of surfactant, and especially, the widest region of it when the content ratio of glycerine to water is at the range of 63-75%. This indicates that increasing of glycerine depressed the hydrophilic property of the surfactant and promoted the formation of microemulsion gel which contains a large amount of oil. Therefore utilizing microemulsion gel which belong to this range, we can apply it to very various products.

On the contrary, it becomes turbid and the hardness is getting down when the content ratio of glycerine to water is over arround 77% and finally we can't get the formation region of microemulsion gel when the content ratio of glycerine to water is over around 83%. The result of the above-mentioned experiment is shown in Fig.3 using the tetrahedral-phase diagram in three-dimension.

From those all experiments, the mutual relation of each ingredient can be summarized as follows.

i) The increasing of oil content makes the clarity of microemulsion gel down and makes hardness high.

ii) The increasing of surfactant content makes the clarity of microemul-

sion gel enhanced, makes hardness high, and makes pick-up status bad.

iii) As the content ratio of water to glycerine is getting increased, hardness is getting higher, and resonance effect becomes enhanced.

iv) As the content ratio of glycerine to water is getting increased, hardness is getting lower, and clarity becomes enhanced.

v) As the content of water phase(glycerine, water) is getting increased, hardness is getting lower and pick-up status becomes better.

3-2. Application of Microemulsion Gel

1) Cleansing products.

Cleansing is the most fundamental product in skin-care process. It removes any impurities and make-up residues on the skin and plays an important role of keeping clean and healthful skin.

Generally it is very difficult to cleanse completely oily impurities such as make-up residues by surfactant types of cleansing products or soaps. They can be usually removed by using solvent types of cleansing cream. However, it is not easy to remove the inner impurities of pores or furrows of the skin with solvent type of cleansing cream. Furthermore, the skin can be rough when it is done tissue-off after cleansing cream.

These kinds of problems can be simply solved when we use microemulsion gel type of cleansing product. When applied to the skin, it dissolves oil-based impurities easily due to its bicontinuity. Besides, the evaporation of water by light massage occurs phase transition(O/W→W/O) and the solubility of oily impurities increases. On the process of rinse off,

the influence of glycerine, which makes the surfactant more hydrophobic, is reduced by the further addition of water and thus the system dissolving oily impurities creates phase retransition (W/O→O/W) and fine emulsion droplets. The fine emulsion droplets with impurities even from pores and furrows of the skin can be easily rinsed off with water.

The formation regions of microemulsion gel which can be used to microemulsion gel type of cleansing product are shown in Fig. 4.

2) Hair dressing products.

Hair dressing product is used for giving setting effect and brilliance on hair. It provides hair healthful and neat condition by supplying water and oil Hair dressing products can be largely divided into oil & wax type, aqueous type, emulsion & solubilization type and aerosol type.

These kinds of products have both merits and demerits of their own respectively, i.e, when setting effect shows excellency, the property of rinse off can be bad and hair damage can be caused, while the property of rinse off is excellent when setting effect shows bad.

Applied in hair dressing products, microemulsion gel can provide emolliency to the scalp, good hair-holding qualities and moisturizing properties with oil and polyol, and the satisfactory property of rinse off with its own surfactant.

As shown in Fig. 5, it can be applied to the variously product for oily, dry and normal type of hair arranging the oil content between 40～60%.

3) Others.

Besides the above-mentioned product, it can be better to utilize fine microemulsion gel on the prescription where we want to make active ingredients absorbed into skin much more and more quickly. It can be also applied to the products such as perfume gels, emollient body preparations, hand creams, and sunscreens.

4. Conclusion

In this study, we have investigated the optimum conditions for microemulsion gel formation, in the view of superior consistency, stability, clarity and pick-up by elucidating the influence of polyol on microemulsion gel which is made of nonionic surfactant, oil and water. Glycerine which is triol is the most suitable coupling agent of all studied polyols. The variation in the content of water and glycerine has major influence on the microemulsion gel system adding glycerine and the optimum formation region of microemulsion gel is the widest when the ratio of glycerine to water is 63～75%.

Those results can be expected to utilize for the product development as the fundamental data when the proper ratio of oil and surfactant is selected according to the required function for product characteristics.

Especially it is believed that optimum use of polyol seems to be helpful to obtain the microemulsion gel containing maximum amount of oil phase with minimum amount of surfactant, which is recently one of the major problems of cosmetic chemists.

However, it is needed to experiment on more various kinds of oils and surfactants because we may get unsatisfactory feeling on the applied

products of microemulsion gel in just accordance with this experiment since we didn't test with many different oils and surfactants. In conclusion, it is expected to manufacture microemulsion gel product of more excellent quality based on the result of this experiment.

요 약

이 논문은 외관, 안정도, 얇고 균일하게 끈적이지 안는 Film 형성등의 우수한 특징을 갖고 있기 때문에 Cosmetic preparations의 여러 방면에 응용하고 있는 Microemulsion gel에 관한 것이다.

우리의 연구는 Microemulsion의 Clarifying agent 또는 Coupling agent로 이용되고 있는 Polyol류가 Microemulision에 미치는 영향을 해명함으로써, Consistency, Stability, Clarity, Pick-up from a container등이 우수한 최적의 Microemulsion gel의 형성 조건을 확립하여 Cosmetic preparations에 응용할 수 있도록 하는 것이다.

연구한 System은 De-ionized water, Oil로는 Polar한 Ester oil, Emulsifying agent는 Nonionic syrfactant, Coupling agent는 Polyol로 구성하였으며, Three component phase diagram과 Tetrahedral phase diagram을 이용하여, Polyol의 비율에 따라 Microemulsion gel의 투명 영역, Consistency, 충격에 의한 Resonance 효과, Pick-up from a container등의 변화를 고찰하였다.

연구결과 구성 성분중 De-ionized water의 Coupling agent의 비율변화에 의한 영향이 가장 크게 나타났으며, Coupling agent로 사용된 Glycerine의 물에 대한 비율이 63~75%일때 최적 Microemulsion gel 형성 영역이 가장 넓게 나타났다.

특히 Polyol의 비율을 적절히 선택함으로써, 최근 관심이 모아지고 있는 최소의 유화제량으로 최대의 유상량을 함유한 Microemulsion gel을 얻는데 기여할 수 있을 것으로 생각된다.

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Table Ⅰ. Composition

	A	B	C	D	E
O.P	20%	30%	40%	50%	55%
POE(25)ODE	35%	30%	25%	20%	15%
Water	35%	20%	15%	10%	10%
Polyol	10%	20%	20%	20%	20%

Table Ⅱ. *Comparative experiment result of polyols*

Type	Polyol	A		B		C		D		E	
		M.G	Clarity	M.G	Clarity	M.G	Clarity	M.G	Clarity	M.G	Clarit
diol	Propylene Glycol	○	+	○	+	○	+	x	.	x	.
	3-Methyl-1,3, -Butanediol	○	+	○	+	○	+	x	.	x	.
	1,3-Butylene Glycol	○	+	○	+	○	+	x	.	x	.
Over triol	Glycerine	○	+++	○	+++	○	+++	○	+++	○	+++
	Sorbitol	○	+++	○	+++	○	++	○	++	○	+
	Malbit	○	+++	○	+++	○	++	○	+	○	+

1) M.G : The formation of microemulsion gel (○; formation of gel, x; split or no formation of gel)
2) Clarity (+++; transparent, ++; translucent, +; opaque)

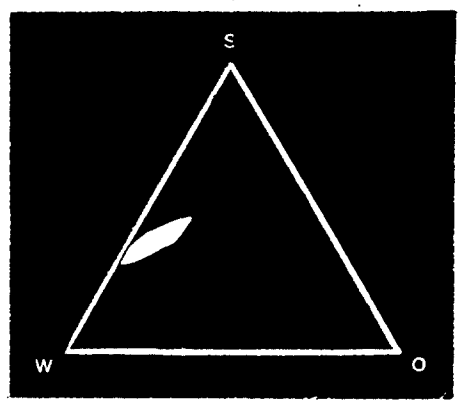
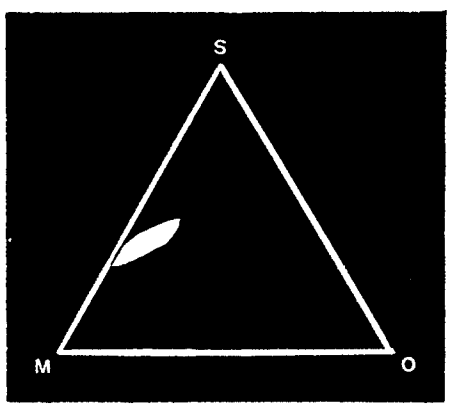


Fig. 1. Formation region of microemulsion gel of the system of POE(25) ODE/ OP/ Water.
(S ; POE(25) ODE O ; OP W ; Water.)

i)



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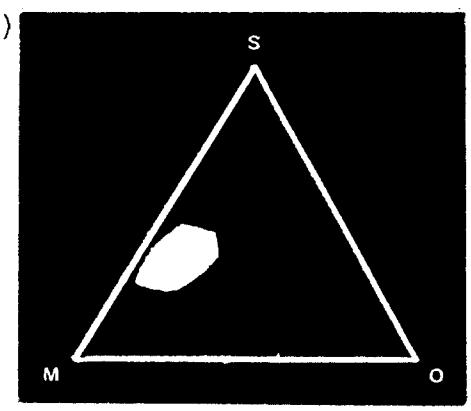

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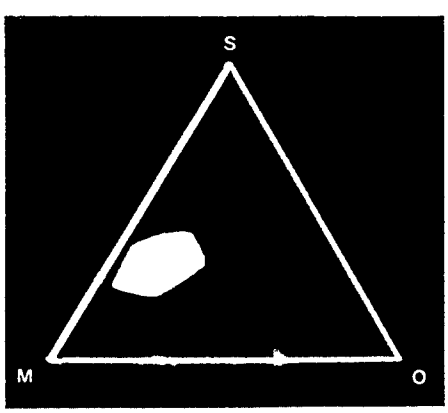

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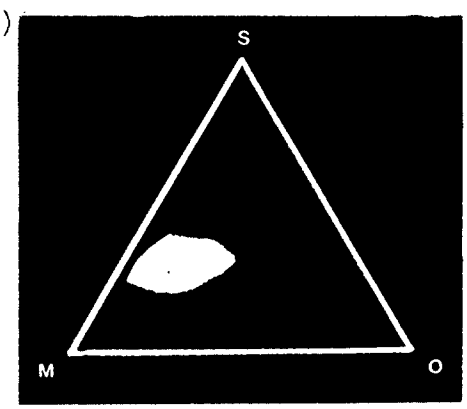

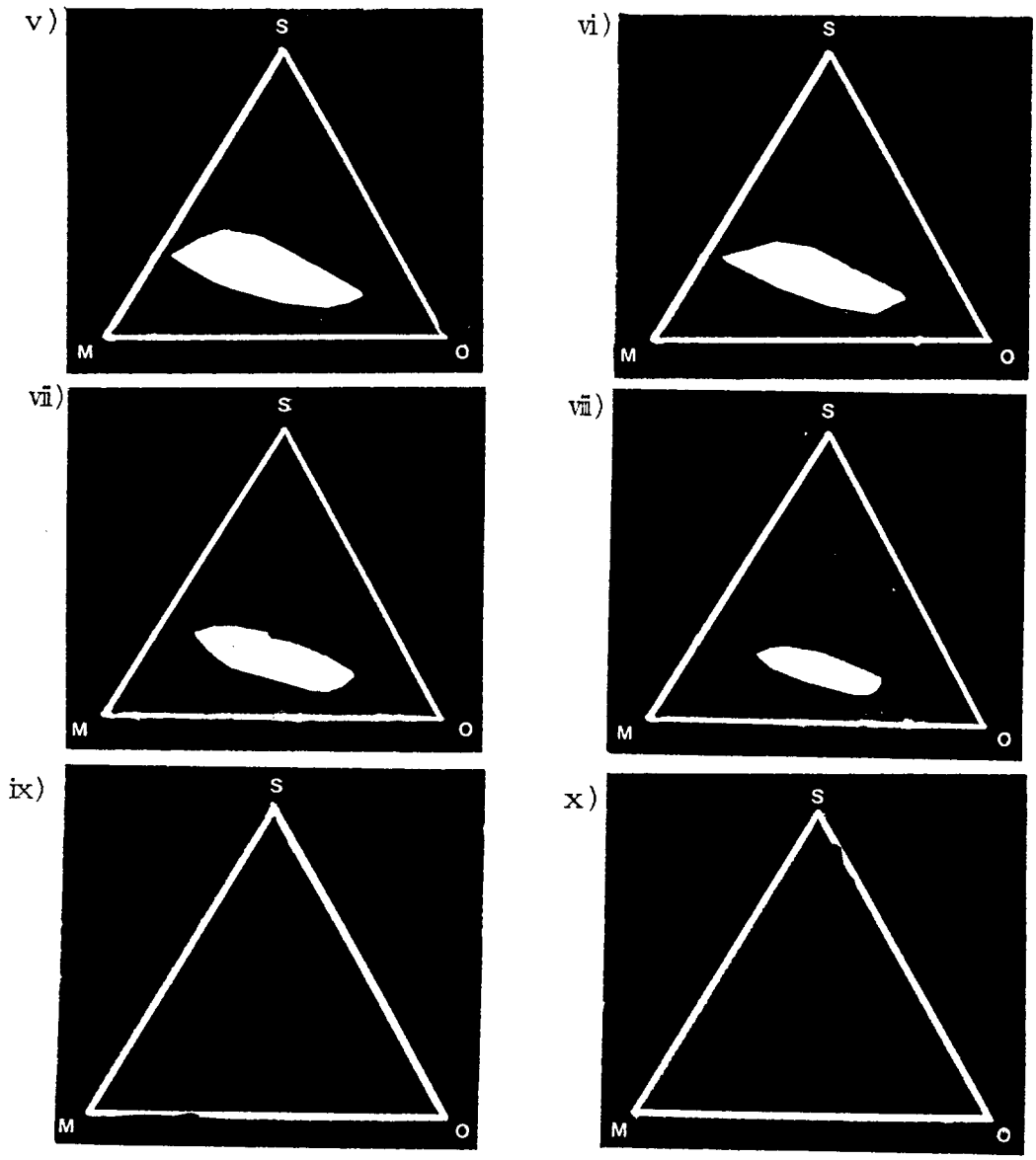

i) M : Water / Glycerine =100/0
ii) " = 83/17
iii) " = 67/33
iv) " = 50/50
v) " = 37/63

vi) M : Water / Glycerine = 33/67
vii) " = 30/70
viii) " = 23/77
ix) " = 17/83
x) " = 0/100

Fig. 2. Three-component phase diagram
(S ; POE(25) ODE, O ; OP, M ; Mixture of Water / Glycerine)

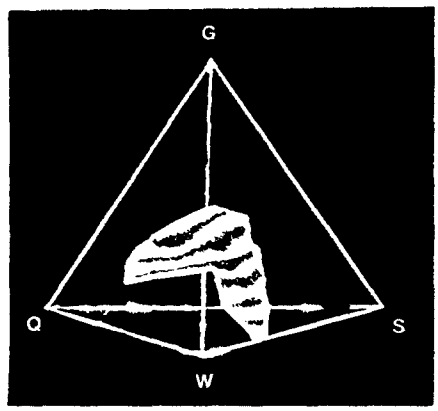

Fig. 3. Tetrahedral-phase diagram
(S ; POE(25) ODE O ; OP G ; Glycerine W ; Water)

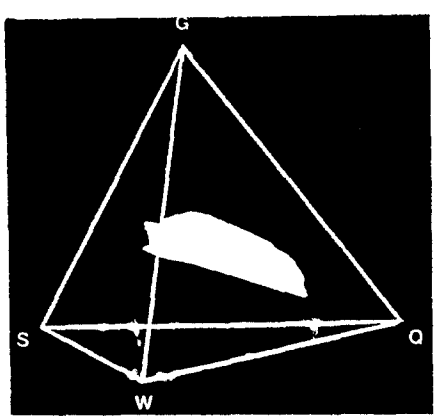

Fig.4. Usable regions of microemulsion gel type of cleansing product.

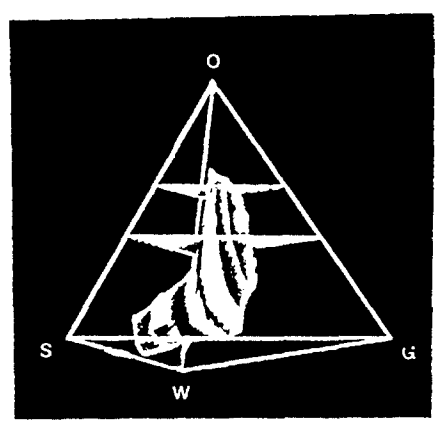

Fig.5. Formation regions of microemulsion gel which can be applied to the hair dressing products.