Application of Water-Holding Polymers as a Skin Moisturizer

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Some water soluble polymers formed "hydrogel" film containing water. This "hydrogel" film was expected to provide natural protective characteristic not found in commonly used low-molecular weight humectants. Film strength and elasticity tests on the polymers gave sodium hyaluronate the highest values under all test conditions.

In vivo tests, surface slip resistance measurement indicated that sodium hyaluronate significantly reduced skin friction resistance and thus increased skin smoothness.

Transepidermal water loss, and skin/polymer affinity measurements revealed that some water soluble polymers formed not a completely occlusive but a water-permeable, a dermal respirable film on skin surface.

In vitro and *in vivo* test results suggested that ideal water soluble polymers which would be useful as a skin moisturizer should meet the following conditions; (i) Should have a high molecular weight rather than a low molecular weight. (ii) Should have a component of N-compound for better skin affinity. (iii) Should have a distortion-structure to form a tough and flexible film on skin surface. Sodium hyaluronate having a molecular weight in $6 \times 10^5 \sim 9 \times 10^5$ range fulfilled all of these conditions. The optimum combination of these properties is believed to enhance the skin's natural protective mechanism and is chiefly responsible for its outstanding performance as a skin moisturizer. It was confirmed further that lotions containing sodium hyaluronate had pleasant skin feel and was perceptible at a low level of incorporation by the consumers.

INTRODUCTION

There are many unanswered questions concerning skin's natural protective mechanism. A variety of humectants and of occlusive substances have been used for many years to improve human skin and to protect it against damage, even though the principles underlying these approaches to skin treatment have not been clearly understood.

However, a great deal of recent work has reported a number of interesting facts concerning hydration of the stratum corneum. For instance, it has been found that stratum corneum contains water soluble compounds which are responsible for the wettability, water-holding and absorbing powers of this tissue, and are called collectively "natural moisturizing factors"¹⁾ of the skin.

From all the published studies, it is obvious that neither an occlusive agent alone nor a hygroscopic substance alone would function as an ideal moisturizer. A proper balance of water-absorbing/holding property is essential for an optimum moisturizing performance.

From these points of view, we attempted to develop moisturizing agents that had both the water absorbing and holding properties. This study was to investigate water soluble polymers having moisturizing smoothing, film forming characteristic not found in commonly used cosmetic humectants.

In addition, viscosity and texture are probably important attributes of skin moisturizer. Accordingly, it is necessary that consumer tests by practical preparations should be carried out. The result must be obtained a cosmetically desirable effect.

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EXPERIMENTAL

1. Materials

Table-1. Materials

Type	Name
biological polymers	●soluble collagen (300,000)
	●polypeptide (10,000)
	●sodium hyaluronate (800,000)
	●chondroitin sulfate (75,000)
semi-synthetic polymers	●carboxyl methyl dextran (over 1,000,000)
	●sodium carboxyl methyl cellulose (45,000)
synthetic polymers	●polyoxyethylene glycol (3,300)
	●polyvinylalcohol (80,000)
	●polyvinyl pyrrolidone (40,000)
typical humectants	●glycerol
	●sorbitol
	●sodium pyrrolidone carboxylate

Figures in brackets represent, approx, average molecular weight.

The water soluble polymers and humectants used were cosmetic grade and without further purification. Sodium hyaluronate was extracted from a cockscomb and chondroitin sulfate from a shark cartilage³⁾. Both were over 95% in purity.

2. Procedure

2-1 preparation of facial lotion

The preparation of the facial lotion used during this investigation is shown in Table-2. Each conce-

Table-2. Formula of facial lotion

1,3 butylene glycol	2.0 wt%
polyethylene glycol 400	1.0
ethyl alcohol	8.0
succinic acid	0.018
sodium phosphatic, dibasic	0.06
methyl paraben	0.1
perfume	0.2
(moisturizer)	(0.1 10.0)
deionized water	make to 100.

Figures in bracket are indicated in Table III.

ntation of the water soluble polymers added to the lotion as a moisturizer was mixed in order to eliminate bias by molecular weight, of approx, at the ratio of molecular weight of each polymer to molecular weight of sodium hyaluronate and carboxyl methyl dextran, which are the largest molecular weight. The amounts of each polymer considering molecular weight are listed in Table-3. Glycerol, sorbitol and Na-PCA were mixed in the lotion, respectively, 5.0, 5.0, 1.0 wt% with commonly used amounts.

Table-3. Amounts of each polymer considering molecular weight

soluble collagen	0.3 wt%
polypeptide	1.0
chondroitin sulfate	1.0
sodium hyaluronate	0.1
carboxyl methyl dextran	0.1
sodium carboxyl methyl cellulose	2.0
polyethylene glycol 4000	10.0
polyvinylalcohol	1.0
polyvinyl pyrrolidone	2.0
sorbitol	5.0
glycerol	5.0
sodium pyrrolidone carboxylate	1.0

2-2 Development of measuring methods

In vitro testing.

(i) Determination of water-absorbing property after dehydrating the test materials in vacuo for 48 hrs, 1.0g samples were weighted accurately and moistened with 0.1g of water and kept at 20°C for 24 hrs in air of varying humidity (0%, 28%, 45%, and 80% RH). The amounts of excess water gravimetrically determined at equilibrium condition were plotted on a graph³⁾. From the graph, the water intake at a relative humidity under equilibrium condition was calculated. The lower the boundary value of water-absorbing/holding, the more positive the substance was judged. From the slope of the lines, hygroscopicity was determined.

(ii) Determination of film strength and elasticity

Japanese paper was chosen as a model of substrate available for extensibility test of film. As Japanese paper consists of fibered pulp making up clearly a definite orientation, it is easily broken to give a very small extension toward right angle against the fiber orientation. Each piece of paper measuring 5.0×0.5 cm was cut with scissors and was immersed in 5.0% solution of the polymers or humectants, and kept at 20°C, for 24 hrs under desired humidity (30%, 50%, 80% RH). In this way continuous layer of polymer could be formed within fiber of Japanese paper. Extensibility was measured on a Tensilon/UTM-II (TOYO measuring instruments Co., LTD.) A test piece was clamped between two pairs of jaw and was stretched at a constant rate of extension. The load-extension curve was plotted automatically on a recorder. Typical stress-strain diagrams was obtained by a test piece treated with aqueous polymers. Since Japanese paper materials are never uniform, a large number of individual measurement was necessary.

(iii) Determination of water permeability

We may expect to form a proper occlusive film by a topical application of polymer capable of increasing its resistance to water loss without penetrating into skin. For this purpose, we used a simple device⁴⁾, which utilizes analytical filter paper as a membrane. The filter paper was directly immersed in the lotion, and then substituted its filter paper by a bottle cap, with a complete occlusive cover. The RH below it was maintained at 100% while the upper part was submitted to different atmosphere. The amount of water loss through the continuous layer formed within membrane of filter paper was shown in the ratio of control lotion absent from polymer to lotion containing polymer.

2-3 Development of measuring methods

In vivo testing.

(i) Determination of slip friction resistance on surface

The technique for measuring the slip resistance is described in another paper at this XIth IFSCC International congress⁵⁾ Method of application; the

inner side of the under-arm of the test subject was washed with soap, rinsed with water. The lotion, shown in Table-3, containing polymers or humectants was applied on the area after the skin was dry. After 20 min, the measurement was to determine whether the skin was more or less smooth than the control area to which a lotion not containing polymer or humectant was applied. The load-stroke curve was recorded automatically by an X-Y recorder.

(ii) Determination of transepidermal water loss

Ace Hygrometer (Ace Scientific Laboratory, Model AKE⁶⁾) was used for this measurement. The method includes measuring the increased RH into a fixed, controlled of air enclosing the skin. The method of application is exactly the same as the method used in the determination of slip resistance. After the application of lotion, skin surface water content was measured in the amount of water vapor to change with time by HYGRO THERMOMETER.

(iii) Determination of skin/polymer affinity

The following *in vivo* test was developed for screening of skin/polymer affinity. The inner side of the under-arm of the test subject was degreased, that is washed twice with soap, rinsed completely with water, and warm air from a hair-dryer blown onto the skin. The lotion containing the polymer was then applied to the skin surface. After 5 min, a water droplet from microsyringe was put on the skin surface and the contact angle between water-droplet/skin was immediately measured by microscope. Carefully and gently rinse (showering) the inner side of the under arm with running water. After the area has dried, the contact angle was measured in the same manner again. The initial contact angle was compared with the corresponding value obtained by rinsing with water. The larger the difference between two contact angles, the more negative was the affinity the polymer.

(iv) Dermal respiration

To confirm that some of water soluble polymers did not form a occlusive film, not only water permeability was measured but also dermal respiration. The arm of test subject was directly immer-

sed into the lotion containing the polymer and then by cold air from a hair-drier blown onto the skin for 1 min. The arm was completely wrapped in a sack made of vinyl sheet and the inside air was exhausted by vacuum. After putting the regular air into the sack and maintaining for 20 min, the quantity of CO_2 gas arising from the skin was measured by Kitagawa-style CO_2 gas detector⁷⁾ (KÔMYO-RIKAGAKU Engineering Co.). For the comparison experiment, the lotion containing the polymer was applied to the one arm, and 8% w/w alcohol solution without the polymer was applied to the other arm.

3. Consumer test With lotions

The *in vitro* and *in vivo* tests suggested that Na-hyaluronate was far superior to all other polymers investigated. Na-hyaluronate was chosen and added 0.05%, 0.02% wt respectively to the previous lotion as described and applied on the faces of 118 female subjects for a week. They were asked of their preferences and answered "yes" or "no" on the given question items. The placebo effect and any 'bias' was avoided by employing a blind technique and a randomized method. Statistical analysis of control usage tests were carried out.

Fig.-1. Moisture balance of different polymers and humectants, data obtained substances containing 10% wt water, after 24hrs.

RESULTS AND DISCUSSION

In Vitro tests

Blank showed that at RH of 60% an equilibrium state exist such that the water content of the stratum corneum could not fall under a value of 10 mg/100mg dry wt⁸⁾. This value (10% w/w) is critical level necessary to keep the stratum corneum soft and elastic⁹⁾.

From moisture balance in Fig.-1, it was found that each substance had its own equilibrium humidity for maintaining 10% w/w water content. For instance, Na-hyaluronate has an equilibrium humidity of, of approx., 50% RH. Below this value it gradually releases 10% w/w water added.

Na-PCA, glycerol were judged to be very positive substances but sorbitol, PEG 4000 were negative. From the slope of the lines (Fig.-1), it was found further that biological polymers were not very dependent of humidity change. This is one of the very

Fig.-2. water absorption on 80% relative humidity at 20°C, for a long time.

Table-4. Classification by properties against water

category	under condition of high R.H.	under condition of low R.H.
I	water-absorbing power High	water-holding power Low
II	// Low	// High
III	// High	// High
IV	// Low	// Low

important properties for an ideal moisturizer. In addition, the initial slope shown in **Fig.-2**, indicated that the biological polymers, particularly, Na-hyaluronate absorbed constant amount of moisture at a rapid rate from the environment under 45%, 80% RH respectively. This is a beneficial effect for a moisturizer since it enables the system to read just quickly against changing environment.

A more effective moisturizer would be one which falls into category II class in **Table-4**. It has not only low water-absorbing power under high RH, but high-holding power under low RH. From this point of view also, the biological polymer clearly had desirable properties.

Fig.-3. and **4** showed that Na-hyaluronate for-hyaluronate formed the most flexible and toughest film among the test polymers. The reason is probably that the polymeric structure of Na-hyaluro-

Fig.-4. Maximum stress of each polymer under different relative humidities.

nate is due to the distortion-structure, such as 1,3 glucoside bond and to its extreme large molecular weight. It is expected that this film would be a very thin second skin on natural skin surface and provides a natural protective effect.

Some typical *in vitro* rates of water vapor permeation through continuous layer formed within fiber of filter paper are summarized in **Table-5**. From these data also, as expected, the lotions with

Table-5. *in vitro* water permeation; the amount water loss through continuous layer within filter paper

Substances added to lotion.	Rate (mg/cm ² /h)			Ratio (added/control)		
	0%	45%	80%	0%	45%	80%
Control	1.07	0.90	0.41			
C M D	1.18	0.83	0.30	1.10	0.92	0.73
Na-hyaluronate	1.04	0.89	0.33	0.97	0.99	0.80
Soluble collagen	1.00	0.84	0.35	0.93	0.88	0.90
Polypeptide	0.97	0.79	0.37	0.91	0.88	0.90
Chondroitin sulfate	0.97	0.85	0.34	0.91	0.94	0.83
P V A	1.14	0.80	0.31	1.07	0.89	0.76
C M C	1.17	0.68	0.15	1.09	0.76	0.37
P V P	1.17	0.75	0.33	1.09	0.83	0.80
P E G 4000	1.06	0.84	0.24	0.91	0.93	0.56
Glycerol	1.10	0.78	0.29	1.03	0.87	0.71
Sorbitol	1.13	0.83	0.25	1.06	0.92	0.61
Na-P C A	1.16	0.78	0.34	1.08	0.87	0.83

Fig.-3. Maximum elongation of each polymer under different relative humidities.

the biological polymer not only reduced water vapor loss under condition of different RH. but became, particularly, a small difference as compared with other substance under condition of high RH. The fact is desirable property due to not induce superhydration.

In vivo tests

Most people prefer a cream or lotion that is not oily or tacky. Smoothness is probably an important factor upon product choice. Lotions containing the polymer become very thin and spread evenly while being on the skin. After application is complete, they return to their original texture, protective thickness, and smooth afterfeel.

The results shown in Fig.-5. clearly showed that lotions containing Na-hyaluronate reduce slip resistance. On the other hand, soluble collagen increase it. These results clearly differ from the microphotographs presented by Todd et. al⁹⁾ that soluble collagen is a definite reduction in level of surface roughness and desquamation. This difference is believed to be due to the fact that the skin became

Fig.-5. Slip resistances of each polymer obtained in using 22 women on normal and dry skin subjects.

Fig.-6. *in vivo* water vapor loss through skin surface on 47% relative humidity at 23 °C, changes of application.

heavily moist with soluble collagen, and thus increased the "load" of the polished probe of instrument touching the skin.

Some typical water vapor loss rates through skin are shown in Fig.-6. as a function of time. TWL (transepidermal water loss) reached nearly a constant rate after 15 minutes equilibration.

It is of interest to note that hygroscopic substances such as glycerol, Na-PCA reduced TWL, whereas Na-hyaluronate did not change it when compared with untreated skin. The results clearly confirmed *in vitro* moisture balance data in Fig.-1. and water permeability data in Table-5. Fig.-6. indicated that under 47% RH, glycerol, sorbitol are still effective as a moisturizer, and Na-hyaluronate is thought of not very change as well as natural skin protective property.

It is believed that water-soluble polymers are incapable of penetrating through stratum corneum because of its molecular size and that presumably their application will result in the formation of a layer at or near the very top of the epidermal

structure. Accordingly, the question is whether or not these layer is easily rinsed out. It was shown in slope of curve in Fig.-7. that Na-PCA, Na-hyaluronate, soluble collagen are ones which are absorbed by the corneum so that it is not easily

Fig.-7. *in vivo* affinity between substance and skin; as compared with contact angle of water droplet on skin surface whether or not substances are affinity.

rinsed out. This suggests that the good affinity is due to having N-compound in chemical structure and having a more high molecular weight, except for Na-PCA. The results of. *in vivo* and *in vitro* tests predicted that lotion containing Na-hyaluronate, which had unique balance of water-absorbing/holding power, slip resistance reduction, constant

Fig.-8. Dermal respiration; quantity of CO₂ gas arising from the skin surface.

Fig.-9. Effectiveness of sodium hyaluronate lotion in consumer test. sign test; significance *** at $p=0.01$, ** at $p=0.05$ 118 women completed the test.

TWL, water permeability, might be more effective than lotions containing conventional humectants such as glycerol, sorbitol, or other polymers. The result of the consumer test (**Fig.-9**) showed that this prediction was valid and that Na-hyaluronate was further responsible for its outstanding preference.

In addition, **Fig.-8**, showed whether or not polymer lotions disturb skin physiological action, that is, dermal respiration. It could not understand whether or not the increased dermal respiration is good for dermal physiology. The fact not to change in dermal respiration is believed anyway to be good for natural skin.

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