

## Effects of pH changes in a specific detergent multicomponent emulsion on the water content of stratum corneum

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### Synopsis

The effects of varying pH in a specific detergent multicomponent emulsion showed a greater dehydrative effect at alkaline pH (7.5) than at neutral or acidic pH (4.5). This dehydrative effect was more pronounced among younger than older subjects.

### INTRODUCTION

Blank and Shappirio (1) have demonstrated that the water-binding capacity of the stratum corneum is decreased by detergent solutions. Accordingly, we were able to show in our earlier studies that contact with detergent solutions causes dehydration of the horny layer (3). In the present study, the effect of pH in a specific detergent multicomponent emulsion was investigated.

### MATERIALS AND METHODS

#### GROUPS OF PATIENTS STUDIED

Since earlier studies of our own have shown that the water content of the stratum corneum depends on the age of the subject, we investigated two groups of patients selected according to their age. Group A consisted of 24 female and 16 male subjects, with a mean age of 20.5 years (age range 16 to 43). Group B included 31 females and 9 males, with a mean age of 71.5 years (age range 60 to 86). None of the test subjects suffered from skin diseases.

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Dedicated to Dr. H. Wölcher, Plönheim, on his 70th birthday.

## TEST PROCEDURE

Twenty-four hours before the beginning of the measurements, the test subjects washed their skin according to a standardized procedure. Subsequently, no further washing or application of topical preparations took place. The subjects were acclimatized to ambient conditions (standard temperature 22–24°C, relative humidity 50–55%) for a period of 30 minutes before the start of the investigation.

The moisture content of the stratum corneum was then determined by means of infrared spectroscopy and corneometric assessment of skin capacitance. These measurements were repeated immediately after application of the detergent emulsions and at 30-minute intervals for the following three hours.

## METHODS OF MEASUREMENT

*Infrared spectroscopic studies.* The measurements were made by means of a commercial infrared spectrophotometer with an FMIR attachment (Model 297, Perkin-Elmer Ltd., Beaconsfield, Buckinghamshire, U.K.). The FMIR apparatus consists of a germanium crystal that is applied to the skin. At the surface of contact the infrared ray is reflected 50 times, being partially absorbed at each reflection. The absorption is wavelength-dependent, so that an infrared absorption spectrum can be measured. Three absorption bands are relevant for the determination of the moisture content of the stratum corneum: the amide 1 and amide 2 bands, which are in a fixed ratio dependent only on the proteins present; and the H-O-H scissor vibration of water at  $1645\text{ cm}^{-1}$ , which is superimposed on the amide 1 band. The ratio of absorbances in the amide 1 and amide 2 regions is thus a relative measure of the moisture content of the stratum corneum (5). The results may be slightly distorted by infrared absorption of surfactants within the amide 1 region. This would lead to a slight overestimation of hydrative effects and a slight underestimation of dehydrative effects. The essential findings of this study, namely the measurement of a dehydrative effect, is therefore not attributable to this source of error.

*Skin capacitance studies.* The capacitance of the stratum corneum was assessed with a commercial corneometer (Model CM 420, Schwartzhaupt Medizintechnik, Cologne, FRG). In this method, the stratum corneum together with the hydrophobic foil of the measuring probe form an electrical conduction system. The electrical properties of the stratum corneum depend essentially on its hydration state. The upper 20  $\mu\text{m}$  of the stratum corneum participate in the measurement as a dielectric medium (4,7). Each measurement is the arithmetic mean of five independent determinations.

## DETERGENT EMULSION EMPLOYED\*

Composition		
Cetesol S75 T <sup>®</sup>	Bechumler und Schwarz, D-5420 Lahnstein	35.0
Monoisipropenylammonium laurensulfate 42%		
Cocamidopropyl betain 5%		
Lumpen S <sup>®</sup>	Hensel, D-4100 Düsseldorf	1.0
Potassium coco-hydrolyzed animal protein		
Cetiol HE <sup>®</sup>	Hensel, D-4100 Düsseldorf	1.0
PEG-7 stercerilate		

Marlamide KL<sup>®</sup>  
 Cocamidopropyl  
 Laktolin pH 5.0  
 Sodium lactate  
 Oxypon 288<sup>®</sup>  
 PEG-10 olive  
 Fleur PF 1145  
 Glucamate DC  
 Methyl glucosyl  
 PHB-methyl ester  
 Methylparaben  
 Syngam<sup>®</sup>  
 Ethyl lineoil  
 Amino acids, 1%  
 nicotinic acid  
 Euxyl K 400<sup>®</sup>  
 Methyl dibutyl  
 and phenyl  
 Prilon BD<sup>®</sup>  
 Disodium EDTA  
 Mal-Grün<sup>®</sup>  
 C.I. 47005  
 Oxyne 2004<sup>®</sup>  
 BHT and cinnamic  
 palmitate  
 Water

\* We thank the manufacturer for the detergent emulsion.

By addition of the  
 additional values of 4.0  
 values of 4.0 and 7.0  
 the solution of 7.0 and 7.0  
 The detergent emulsion  
 cylinder containing the  
 the detergent emulsion  
 18 times w/w detergent  
 solution

## STATISTICAL

The U-test is a non-parametric statistical test.

## RESULTS

## COMPARISON OF SUBJECTS

Table I shows the results for group A.

Marlamide KL <sup>®</sup>	(Hüls Chemie, D-4370 Marl)	1.5
Cocamidopropyl lauryl ether		
Lakrolin pH 5.6 <sup>®</sup>	(Böhringer, D-6800 Mannheim)	1.0
Sodium lactate		
Oxypon 288 <sup>®</sup>	(Zschimmer und Schwarz, D-5420 Lahnstein)	1.0
PEG-10 olive oil		
Fleur PF 1145 <sup>®</sup> , perfume oil	(Quest International, D-2000 Hamburg)	0.9
Glucamate DOE 120 <sup>®</sup>	(Nordmann und Rassmann, D-2000 Hamburg)	0.6
Methyl gluceth		
PHB-methylester <sup>®</sup>	(Merck, D-6100 Darmstadt)	0.2
Methylparaben		
Syngam <sup>®</sup>	(Synpharma, D-5100 Aachen)	0.2
Ethyl lineolate and tocopherol		
Amino acids, Vit. B 6, urea phosphate, nicotinic acid		0.12
Euxyl K 400 <sup>®</sup>	(Schülke und Mayr, D-2000 Hamburg)	0.1
Methyl dibromo glutaronitrile and phenoxy ethanol		
Prillon BD <sup>®</sup>	(BASF, D-6700 Ludwigshafen)	0.1
Disodium EDTA		
Mal-Grün <sup>®</sup>	(Dragoco, D-3450 Holzminden)	0.02
C.I. 47005 and C.I. 61570		
Oxyhex 2004 <sup>®</sup>	(Merck, D-6100 Darmstadt)	0.005
BHT and citric acid and ascorbyl palmirate		
Water		53.255

\* We thank Sebapharma GmbH & Co., D-5407 Boppard 1—Bad Salzig, for the preparation of the detergent emulsion.

By addition of NaOH and HCl the pH of the detergent emulsion was adjusted to three additional values, so that four detergent emulsions of the same composition with pH values of 4.0, 5.5, 7.0, and 8.5 were available for the investigation. Before application the solutions were diluted with water in a 1:4 ratio, resulting in pH values of 4.5, 5.9, 7.0, and 7.5 for the detergent solutions used in the test series.

The detergent solution was applied to the skin in a standardized way, using a 590-g iron cylinder covered with terry cloth. The cylinder was immersed in a container filled with the detergent solution and rolled over the flexor side of the forearm from elbow to wrist, 18 times within three minutes. This method ensures an even distribution of the detergent solution over the test area. Subsequently, the skin was blotted with fluff-free paper.

#### STATISTICAL EVALUATION

The U-test or paired difference test of Wilcoxon, Mann, and Whitney was used for statistical significance testing.  $\alpha = 0.05$  was chosen as significance level.

#### RESULTS

##### COMPARISON OF THE MEASURED VALUES FOR UNTREATED SKIN IN GROUP A (YOUNGER SUBJECTS) AND GROUP B (OLDER SUBJECTS)

Table I shows that the moisture content of the untreated stratum corneum was higher for group B (older subjects) than for group A (younger subjects). This difference is

significant for the infrared spectroscopic measurements. For the corneometric assessment of skin capacitance, the difference appears to be a trend but is not significant. Particularly for the values measured by infrared spectroscopy, much greater variability was found in group B (older subjects).

#### IMMEDIATE HYDRATIVE EFFECT ON THE STRATUM CORNEUM AS A FUNCTION OF THE pH OF THE DETERGENT SOLUTION FOR BOTH GROUPS

The results of our measurements are shown in Figures 1 and 2. It is evident from both infrared spectroscopic and corneometric measurements that a hydrative effect was the immediate result of treatment with the solution. The figures show clearly that this effect was significant in nearly all cases. Neither the infrared spectroscopic nor the corneometric measurements showed a statistically significant difference between the individual detergent solutions or between the two groups.

#### DEHYDRATIVE EFFECT OF THE SURFACTANTS AS A FUNCTION OF THE pH OF THE DETERGENT SOLUTION

The results of the measurements are shown in Figures 1 and 2. Following the initial hydration, a more or less pronounced dehydration effect was detectable by both methods of measurement 30 minutes after treatment. This effect lasted at least 90 minutes, and became more pronounced with increasing alkalinity of the detergent solution. The figures show at which times values could be measured that differed significantly from the initial values.

Some significant differences between the individual detergent solutions were also found. For group A, infrared spectroscopy showed significant differences between the effects of the pH 4.5 and pH 7.0 solutions at 30 minutes after application; between the pH 4.5 and pH 7.5 solutions at 30, 60, 90, and 120 minutes; and between the pH 7.0 and pH 7.5 solutions at 30 and 60 minutes. Corneometric measurement of skin capacitance showed significant differences between the effects of the pH 4.5 and pH 7.5 solutions at 60, 90, 120, 150, and 180 minutes, as well as between the pH 5.9 and pH 7.5 solutions at 120, 150, and 180 minutes.

For group B, infrared spectroscopic measurements showed no significant differences. Corneometric measurements of skin capacitance were significantly different for the pH 4.5 and pH 7.5 solutions at 30 and 120 minutes after treatment. For the pH 5.9 and

Table I  
Mean Value and Standard Deviation of Measurements on Untreated Skin in Younger and Older Subjects  
(*n* = 40 for Each Group)

Method	Infrared spectroscopy (moisture factor)	Corneometry (scale divisions)
Younger group	1.1532 0.0382	93.23 5.33
Older group	1.1079 0.0849	95.33 5.84

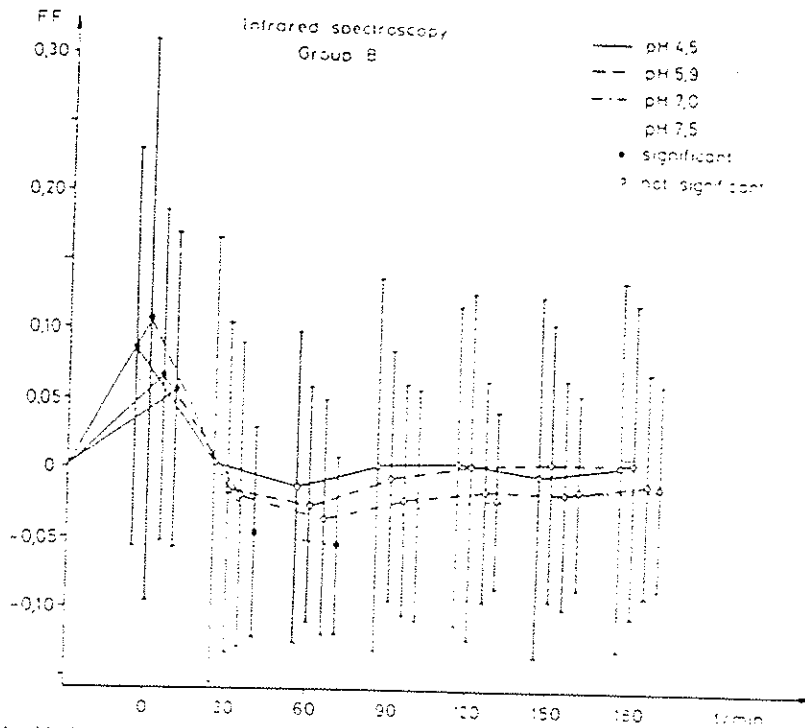
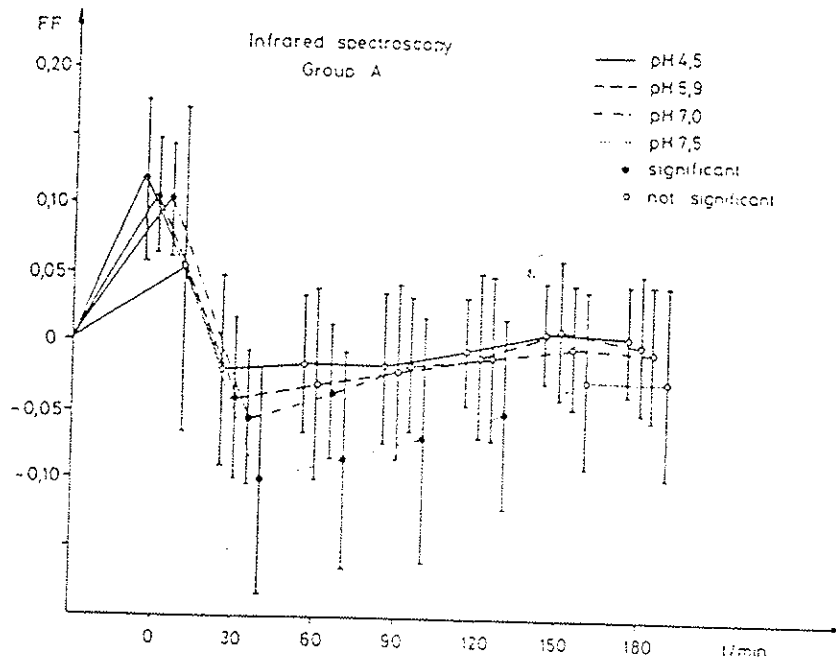


Figure 1. Hydration and dehydration after treatment with detergent solutions of different pH values—  
infrared spectroscopic measurements.

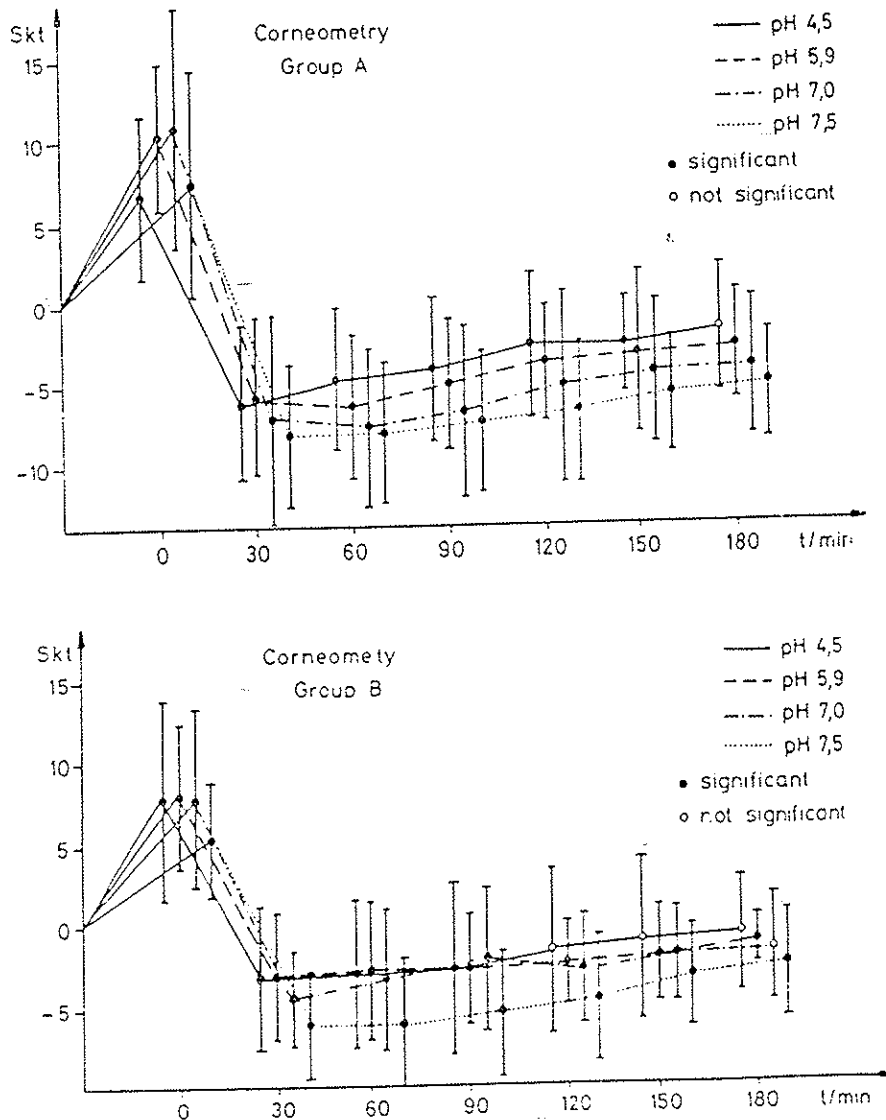


Figure 2. Hydration and dehydration after treatment with detergent solutions of different pH values—corneometric skin capacitance measurements.

pH 7.5 solutions, significantly different effects were measured at 30 minutes, and for the pH 7.0 and pH 7.5 solutions at 90 minutes.

#### COMPARISON OF GROUPS A AND B WITH REGARD TO THE DEHYDRATIVE EFFECT OF THE DETERGENT SOLUTION AT DIFFERENT pH VALUES

Figures 1 and 2 demonstrate that the dehydrative effect was greater in group A (younger subjects) than in group B (older subjects). This difference was significant for the infrared spectroscopic determinations only for the pH 7.5 solution at 30 minutes after treatment. In the case of the corneometric skin capacitance measurements, the following significant differences were found: for the pH 4.5 solution at 30 minutes after treatment; for the

pH 5.9 solution and for the

#### DISCUSSION

In our earlier work (1) we found that the pH of the detergent solution had a significant effect on the hydration of the skin. The pH 4.5 solution caused the greatest hydration, and the pH 7.5 solution caused the least hydration. The pH 5.9 and pH 7.0 solutions had a transient hydrating effect, but this effect was not significant. The dehydrative effect of the detergent solutions was also significant. The pH 4.5 solution caused the greatest dehydration, and the pH 7.5 solution caused the least dehydration. The pH 5.9 and pH 7.0 solutions had a transient dehydrating effect, but this effect was not significant.

No exhaustion of the skin was observed. The pH 4.5 solution had a significant effect on the hydration of the skin, but this effect was not significant in the younger subjects. A notable difference was observed between the younger and older subjects. The younger subjects showed a greater dehydrative effect of the detergent solutions than the older subjects.

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- (7) H. T. ...  
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pH 5.9 solution at 60 and 90 minutes; for the pH 7 solution at 30, 60, and 90 minutes; and for the pH 7.5 solution at 180 minutes.

#### DISCUSSION

In our earlier studies, we were able to show that the water content of the horny layer is higher in older than in younger subjects, showing also higher variability for the former (2). In the present study, the infrared spectroscopic results confirmed the earlier findings. The corneometric skin capacitance measurements showed the same tendency, albeit outside the level of statistical significance. The present studies further show that the application of a specific detergent multicomponent emulsion leads to an initial, transient hydration effect. This hydration effect proved to be largely independent of the pH value of the solution; nor was there any clear dependence on the age of the subjects.

The dehydrative effect of detergent substances is well known. Blank and Shappirio (1) were able to demonstrate that the water-binding capacity of the stratum corneum decreases after the application of detergent substances. In earlier studies (3), we showed that both a soap solution and a surfactant solution caused a considerable dehydration of the stratum corneum. These studies involved infrared spectroscopy measurements as well as corneometric determinations of skin capacitance. These earlier findings appear to be corroborated by the present results.

No exhaustive study on the dependence of the dehydrative effect of detergent solutions on their pH exists in the literature. In the older literature, it was often presumed that soaps had rather a moisturizing effect while synthetic surfactants had a dehydrative effect. Our earlier studies (3) have already disproved this concept. The present studies demonstrate that the dehydrative effect of this particular slightly alkaline detergent emulsion can be more pronounced than that of the same composition at neutral or slightly acid pH. If this result is generally applicable, slight acidification of detergent solutions would be a reasonable strategy to minimize dehydrative effects. This possibility should be explored in more depth.

A notable aspect of the present study was the difference between the groups of older and younger subjects. Although the dehydrative effect was apparent as a tendency in both groups, it was more pronounced among the younger subjects than among the older subjects.

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