Adsorption of Polymer JR on Keratinous Surfaces—PART II

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Synopsis—Data are presented for the adsorption of POLYMER JR from aqueous solutions on BLEACHED and BROWN HAIR, PIGSKIN, and CALFSKIN. The process of adsorption is characterized by a fast uptake in short periods of time, followed by a continuing pickup, which may take over a week to reach equilibrium. Adsorption is also greatly influenced by the presence of surfactants, as can be demonstrated by model shampooing experiments. The data are consistent with a mechanism involving penetration of polymer into the hair shaft or inner layers of the stratum corneum.

INTRODUCTION

Following the development in these laboratories of Polymer JR, which is a cationic cellulose ether derivative (1), a considerable amount of work has been carried out on the adsorption characteristics of this polymer on various surfaces including the keratinous substrates, hair, and skin. The polymer has gained acceptance as an ingredient in commercial shampoos in view of certain beneficial properties it confers on hair, such as manageability, ease of combing, etc. In order to provide information about such applications, this paper

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will report data on the adsorption of Polymer JR onto human hair from simple aqueous solution, and also from a number of aqueous surfactant solutions of potential interest as shampoo ingredients, under conditions simulating shampooing in practice. Results on the adsorption of the polymer *in vitro* onto various mammalian skin stratum corneum surfaces are also reported, together with electron microscopic (EM) results of skin washed with soap with and without the polymer.

<p style="text-align:center">EXPERIMENTAL</p>

Bleached and virgin-brown human hair was obtained from DeMeo Bros.* For adsorption experiments, small swatches weighing 100 mg each were cut and placed in 1-oz counting vials. Ten ml of a water solution of radio-tagged Polymer JR were pipetted into the vials, were left there to contact the hair for a given time, and then the solution was poured off. The hair was then given a brief rinse with distilled water, which was sufficient to remove any entrained radioactive solution. The hair was dried to remove excess moisture, and dissolved with 1 ml of Unisol† tissue solubilizer. This was followed by addition of 0.5 ml of methanol to solubilize any water present and 10 ml of a toluene-based scintillation liquid. The vials were then counted by the normal scintillation method. Counts at 100 per cent efficiency were calculated by a tagging procedure involving addition of small amounts of a standard radioactive toluene sample.

For the shampoo experiments, 5 g of hair tresses were washed with 2 g of shampoo for 30 to 45 sec, and rinsed 3 times in 1 l. quantities of 40°C tap water. The wash/rinse was repeated, and the tress was then dried. The shampoo, rinse, and drying treatment was repeated for the desired number of cycles. The amount of polymer on the hair after a given shampoo cycle was determined by weighing 100 mg of hair into a counting vial and dissolving and counting in the manner outlined above for the adsorption experiments. Each shampoo consisted of a 15 per cent solution of the surfactant, 2 per cent of a fatty amide (Onyx Super Amide L-9C), and 1.5 per cent of Polymer JR 400. The surfactants used were as follows: Tergitol® 15-S-9:‡ 9 mole ethoxylate of a secondary C_{11} to C_{15} alcohol; Miranol CM-SF:δ a dicarboxylic coconut imidazolinium derivative; Standapol T:** triethanolamine lauryl sulfate; Standapol AB-45:** lauryl dimethyl betaine; Standapol ES-2:** sodium salt of the

sulfated 2-mole ethoxylate of lauryl alcohol; F-90:[*] sodium salt of linear do-
decyl benzene sulfonate; and potassium laurate: made in the laboratory by
neutralization of lauric acid[†] with potassium hydroxide.

In the case of the skin, samples of mammalian stratum corneum were pre-
pared in our laboratory from whole skin. For the porcine membranes we used
hairless fetal pigskin which was obtained frozen.[‡] Upon warming, the stratum
corneum layer could be peeled readily by hand from the whole skin. In the
case of calfskin, the starting material was dehaired pickled calfskin.[δ] The skin
was hydrated by soaking it in water overnight and by putting it into a solu-
tion of 0.2 per cent trypsin, 2 molar urea, and 0.1 per cent tris (hydroxymeth-
yl) aminomethane. This solution was then warmed for about 4 hours to 50°C.
At the end of this period, the stratum corneum could be worked off by hand
with some difficulty. Treatment with radio-tagged Polymer JR was the same
as described previously for the hair samples.

RESULTS AND DISCUSSION

Adsorption of Polymer JR on bleached hair was determined for 0.1 per cent
concentration. The data are given in two figures because of the wide range of
time involved; Fig. 1 is in hours, Fig. 2 in days. It can be seen that there is a
fast initial reaction leading to nearly 1 per cent pickup in an hour; however,
attainment of equilibrium takes at least a week. Such a lengthy process differs
from the behavior of polymers on typical inorganic substrates like glass, metal,
and powdered oxides. In such cases, adsorption is largely completed in less
than an hour. It is interesting to note that Polymer JR shows relatively fast
and limited adsorption on clean glass slides (2); hence, there is a presumption
that the character of the hair substrate is responsible for the slow adsorption
in Fig. 2.

An investigation of the literature shows precedents for this, although little
has been reported specifically for the action of polymers on hair. An earlier
study, which has features in common with our results, is the work of Scott and
coworkers (3), who measured the adsorption of cetyltrimethyl ammonium
bromide on natural and bleached hair. Under conditions of acid and neutral
pH, a continuing adsorption was observed, which did not reach equilibrium
even in 24 hours. Their results on bleached hair and 0.1 concentration are
shown by the dotted line in Fig. 1.

[*]Pilot Chemical Co., Los Angeles, Calif.
[†]Matheson, Colman and Bell, Rensellaer, N.Y.
[‡]PelFreez, Rogers, Arkansas.
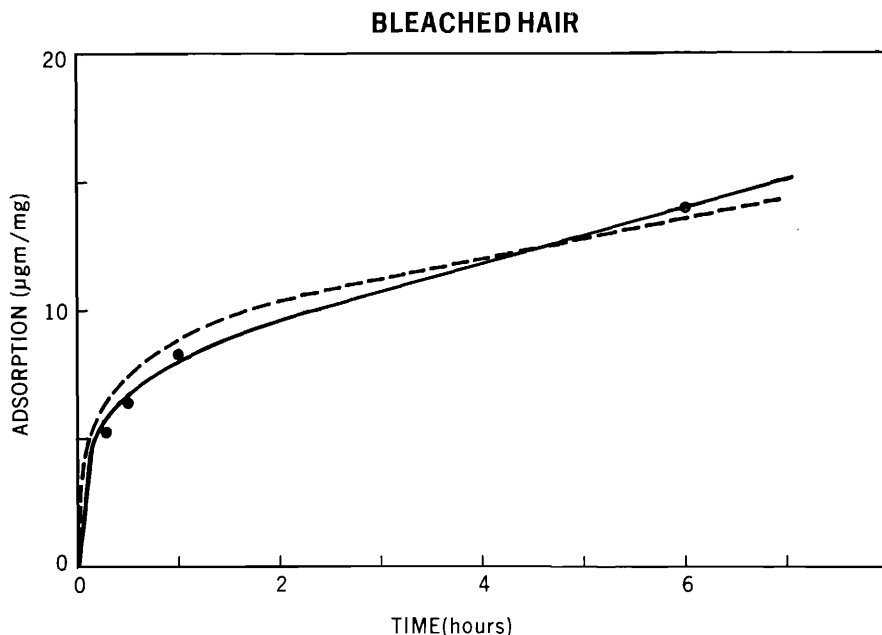[δ]Barrett Corporation, Newark, N.J.

BLEACHED HAIR

Figure 1. Adsorption of Polymer JR-125 on bleached hair (0.1 per cent aqueous solution). Dotted line corresponds to data for adsorption of cetyl trimethylammonium bromide on bleached hair, from (3)

Woodard (4) has provided data on the sorption kinetics of a quaternized polyethylene-imine polymer on virgin brown hair and on bleached hair, but only for times up to 60 min. Allowing for the higher concentration used (5 per cent), her data are similar to ours. Still another study, which should be noted, is the one of Finkelstein and Laden (5), who observed equilibrium times of several days for cationic surfactants on hair by a radio-tracer method.

The relatively large amount of adsorption that is shown here calls for an explanation. Undamaged hair has a BET area of 0.04 sq m/g, a value about equal to the calculated geometrical area (6). Bleached hair has a somewhat larger BET area, about 0.1 sq m/g (2). If one makes the admittedly simplistic assumption that the Polymer JR molecules are stretched out flat on this surface, a monolayer would account for only about 0.1 μg polymer per milligram of substrate. The level actually reached is much greater than this, so one must postulate considerable multilayer adsorption of some kind of penetration into the hair shaft. Although conclusive data do not yet exist, we favor the latter hypothesis. For one thing, adsorption of Polymer JR on glass surfaces (2) is only a small fraction of that on bleached hair (expressing both on an area basis). In the case of glass, equilibrium is apparently reached in a few min-
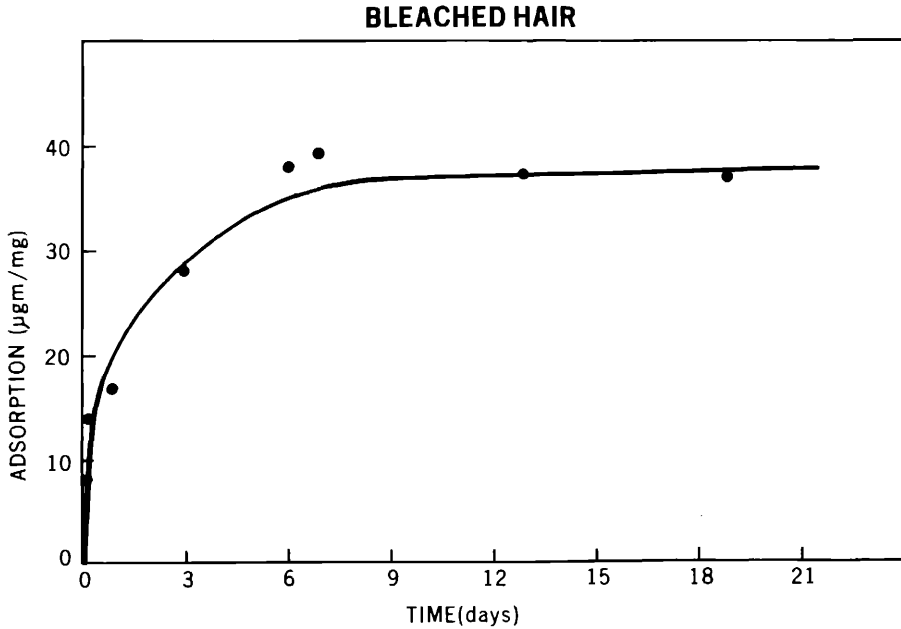
BLEACHED HAIR

Figure 2. Adsorption of Polymer JR-125 on bleached hair (0.1 per cent aqueous solution)

utes. The great length of time required to reach equilibrium for adsorption on hair suggests that a slow diffusion into the substrate is occurring. Indeed, such penetration was demonstrated for the cationic surfactants studied by Scott and coworkers (3).

Because Polymer JR is normally used in the presence of large amounts of surfactants, it was of interest to examine the effect of such materials on the adsorption of the polymer. An example is given in Fig. 3, which shows the effect of adding Tergitol 15-S-9, a nonionic surfactant. Some decrease in adsorption is noted at low concentration (1 per cent), but it requires a fairly large amount (10 per cent) before there is a significant effect. The decrease seen could be connected with modification of the hair by adsorption of surfactant, or by weak association of the polymer with the surfactant micelles.

A more detailed picture is available from the simulated shampooing experiments, whose results are contained in Figs. 4 and 5. Widely varying results are seen for different systems. These concentrates, which have a high excess of surfactant over polymer, were all clear in appearance, as would be predicted from the results of Part I (Vol. 26, no. 9, Pp. 461-475, Sept. 1975). A summary of the precipitation patterns, which were observed for those surfactants not employed in Part I of this paper, is given below. Table I records the appear-
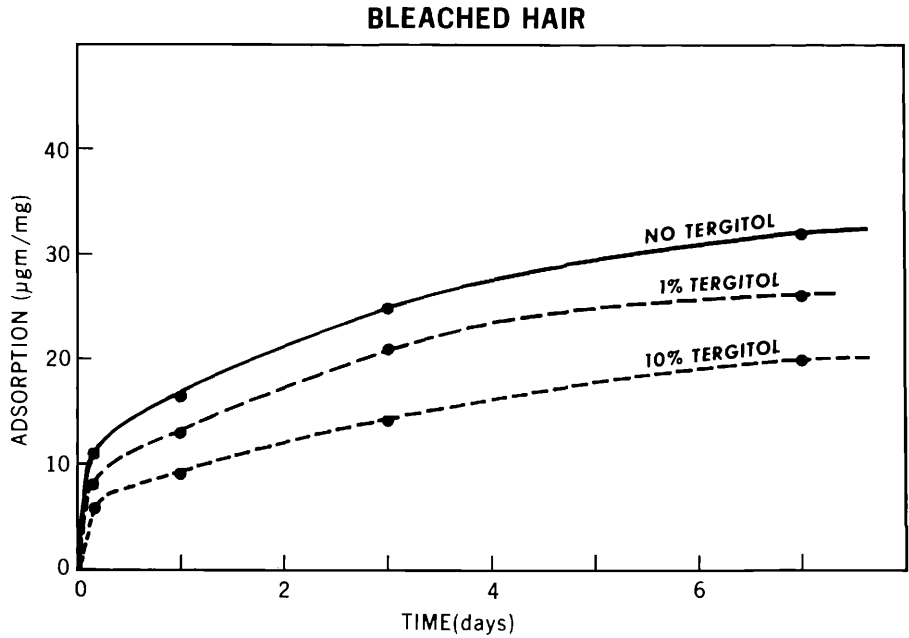
BLEACHED HAIR

Figure 3. Effect of Tergitol 15-S-9 surfactant on the adsorption of Polymer JR-125 on bleached hair
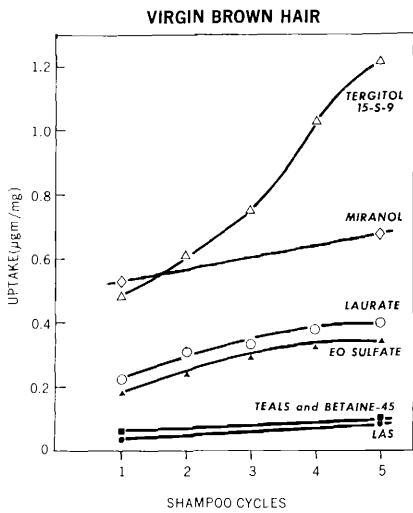

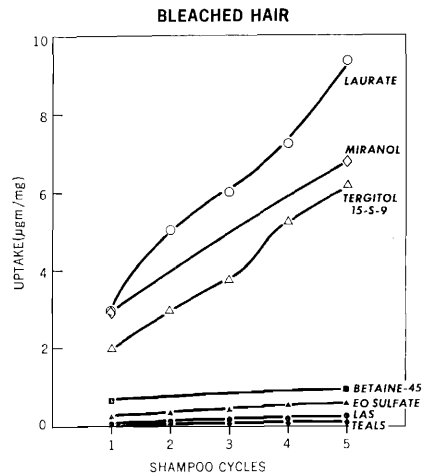*Figure 4.* Deposition of Polymer JR-400 on brown hair from shampoos containing different surfactants

Figure 5. Deposition of Polymer JR-400 on bleached hair from shampoos containing different surfactants

Table I

Appearance of Solutions

Surfactant	Surfactant/Polymer JR Ratio[a]						
	15:1	5:1	3:1	2:1	1:1	1:2	1:4
Standapol AB45	C	C	C	C	C	C	C
Standapol ES-2	C	SP	P	P	P	*P*	P
Miranol (pH7)	C	C	P	*P*	*P*	P	SP
F-90		C	C	C	P	*P*	SP

[a]Polymer JR concentration constant at 1%: P stands for precipitate; *P* stands for heaviest ppt; SP stands for slight ppt; C stands for clear.

ance of distilled water solutions containing 1 per cent Polymer JR to which different amounts of surfactant had been added. On dilution (ten- or twenty-fold) of the 7 shampoo concentrates themselves with the tap water used for rinsing, only the Miranol and the laurate systems developed visible precipitates, the laurate yielding a particularly heavy one.

With virgin brown hair (Fig. 4), the deposition of polymer was lowest for the systems containing Standapol T, F-90, and Standapol AB-45 (pH 6). Deposition increased with Standapol ES-2 and more so with potassium laurate. The pH of this latter system was adjusted to 10. Miranol (at pH 7.5) and Tergitol 15-S-9 caused the greatest deposition of Polymer JR.

With bleached hair, the deposition was about the same for triethanolamine lauryl sulfate, sodium dodecylbenzene sulfonate, lauryl dimethyl betaine, and the sodium sulfate of the lauryl alcohol ethoxylate; all of these gave less than 1 μg of polymer per milligram of hair after 5 cycles of shampooing, and the deposit was scarcely visible by scanning electron microscopy (SEM) (Fig. 6). Considerably more polymer was brought down by Tergitol 15-S-9 and Miranol, *viz.*, about 5 μg/mg of hair, and the latter was readily visible by SEM. The greatest deposition occurs with potassium laurate—over 10 μg/mg. The deposition in this case appears as a nonuniform layer covering the hair scales by the SEM technique (Fig. 7); most likely it consists of precipitated calcium soap together with Polymer JR. This result is of interest in light of the similar deposition on skin found from soap bars with Polymer JR, referred to as follows.

Skin

The adsorption of Polymer JR on skin shows the same general behavior as on hair: a sharp uptake at short times, followed by a slower process that takes at least a week to reach equilibrium. Fig. 8 shows the experimental data at 0.1 per cent concentration for stratum corneum of fetal pig and calf. On a
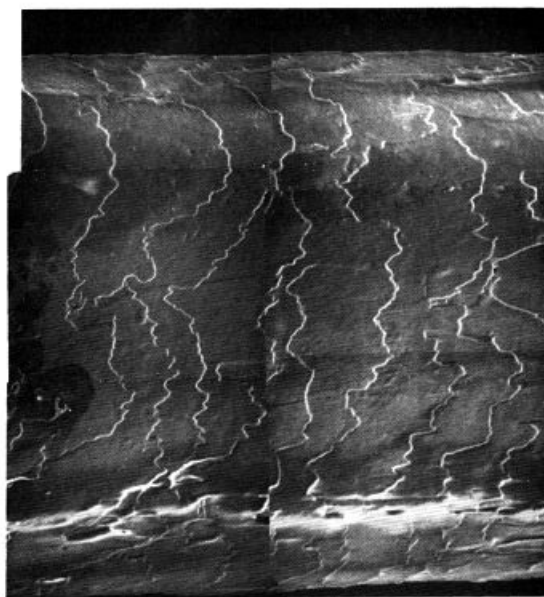
Figure 6. Micrograph of 3000 X of bleached hair, representative of clean hair and hair washed 5 times in low depositing shampoos
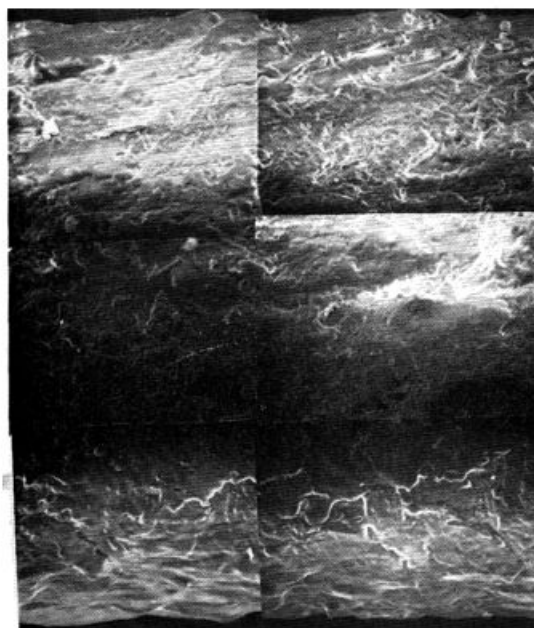

Figure 7. Micrograph of bleached hair, after 5-cycle shampooing with Polymer JR and potassium laurate
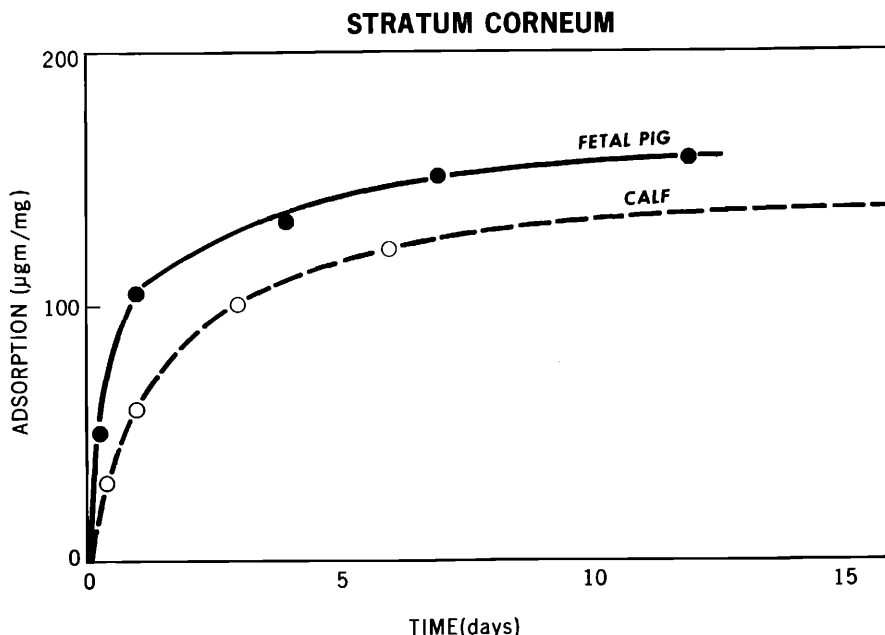
STRATUM CORNEUM

Figure 8. Adsorption of Polymer JR-125 on mammalian stratum corneum

weight basis, the amount adsorbed is considerably larger than for bleached hair, reaching over 10 per cent for both animal substrates.

Like the results for hair, these data are consistent with a mechanism involving slow penetration of the substrate by the polymer. Existing data in the literature support this interpretation. For example, Harrold and Pethica found that large amounts of anionic surfactant could be taken up by powdered epidermal keratin (7); while Choman (8) showed that very appreciable swelling occurs in calfskin exposed to anionic surfactant—an indication of penetration by the surfactant. Only qualitative data seem to be available for cationic surfactants (9, 10); these species are very quickly and tightly bound to skin. The only work specifically on polymer adsorption known to us is that of Cooperman (11), who determined the substantivity of protein hydrolyzates to human stratum corneum by *in vivo* and *in vitro* methods. The polymers used were in the molecular weight range 1000 to 10,000. Kinetics were not followed, but considerable adsorption occurred in 10 min, and it was shown by stripping experiments that the polymers penetrated well into the skin.

The magnitude of deposition on skin suggests that a beneficial effect might be obtained by a barrier or coagulation effect, for example, against penetrating surfactants. We have, in fact, obtained some qualitative visual evidence

Table II

Average Skin Dryness Scores

Group	Time (days)				
	0	7	14	21	28
1 (0% JR)	1.18	3.31	3.17	4.50	4.67
2 (1% JR)	1.25	2.50	2.99	4.22	4.07
3 (2.5% JR)	1.42	3.10	2.90	3.06	3.21

for such an effect, obtained by applying Polymer JR from soap bars.* The bars, of standard 80/20 tallow/coconut-base composition, were made with 0, 1, and 2.5 per cent Polymer JR-400. In a small-scale laboratory test, in which panelists were given a control bar and a bar containing 1 per cent polymer to use under normal conditions for a week, there was a 2:1 preference in skin "after-feel" for the experimental bar. The perceived improvement in skin feel was correspondingly greater for bars containing 2.5 per cent Polymer JR, and this was confirmed in a larger-scale test involving 100 panelists.

For more quantitative assessment of skin condition, the bars with 0, 1, and 2.5 per cent Polymer JR were submitted to Hill Top Research, Inc.† for home use panel testing during the winter of 1974/1975. A panel of 54 women, with a history of wintertime hand chapping, was divided into 3 groups of 18 so as to give an approximate balance of initial hand dryness scores among the test groups. After a week of preconditioning, in which a standard soap and hand lotion were used, the hands were scored for skin condition. Thereafter, the panelists were given the experimental bars, each group having bars of one particular level of Polymer JR, for use at home without any application of lotion. Scores after 0, 7, 14, 21, and 28 days are given in Table II. They were based on skin ratings of 0 through 11, ranging from smooth and soft skin (score 0) through different degrees of flaking, cracking, and fissuring, to severe fissuring (score 11).

After both 21 and 28 days, group 3, using the 2.5 per cent Polymer JR bar, showed a level of skin dryness significantly ($P = 0.05$) less than that shown by group 1 using the control bar. Directional trends also indicated an improvement for the 1 per cent JR bar over the control, as well as a reduction of fingernail splitting for both polymer-containing bars.

Supporting visual evidence for the previous results was obtained by comparing the skin condition of a female subject, who had washed her hands 3 times during 1 hour intervals with a commercial soap, and then 3 times there-

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after at hourly intervals with a 1 per cent Polymer JR bar. The skin was repli-
cated using the technique of Facq *et al* (12) after completion of the first 3
washings and then again after the second group of 3. SEM revealed a smooth-
ing of the skin structure after the second series of 3 washings, as well as the
presence of deposited material.

Conclusion

It has been shown that substantial adsorption of Polymer JR occurs on both
hair and skin. The size of the uptake far exceeds that expected for simple
monolayer adsorption onto the outside surface of these keratin substrates, and
indicates that penetration of the polymer into these (porous) substrates does
occur. Consequences of such penetration include possible barrier effects
against surfactants and moisturization effects.

While it is not possible to rationalize fully the observed results on adsorp-
tion and deposition in terms of the interaction patterns presented in this
paper and in Part I, certain guidelines do emerge. On the one hand, the surfac-
tant-polymer systems exhibiting highest deposition on hair, included a "non-
interacting" surfactant (Tergitol 15-S-9), as expected, but also the "interact-
ing" surfactants potassium laurate and Miranol. The precipitates developed
by the latter shampoos on dilution evidently promote adsorption of the poly-
mer, and, possibly, the high pH of the soap has an effect. On the other hand,
much lower adsorption was obtained with the other "interacting" surfactants,
and this evidently results from the modified nature of the polymer in these
solutions (see Part I of this paper). One anomaly, currently under study, is
the low uptake observed with the other "noninteracting" surfactant, *viz.*, the
betaine. A possible factor in this case is that this surfactant itself adsorbs on
the keratin, and in this way influence the adsorption of the polymer.

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