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Polyurethane Linings for Steel Fuel-Storage Tanks

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Polyurethanes are among the few types of organic materials which are suitable for use in coating form as linings for large, steel fuel-storage tanks. Such linings have been in service in shore tanks of the Navy for five years, and have given satisfactory performance. However, in the bottom areas, where the linings are exposed to water, blistering has occurred. The blisters are tough, liquid-filled hemispheres, which generally develop within the layers of the coating.

Upon the basis of numerous immersion experiments, it is suggested that there are sites within polyurethane coatings which are particularly subject to blister initiation. Evidence has been collected to indicate that these sites may be minute, carbon dioxide bubbles formed by side reactions of the coating components. Several means of reducing the numbers and sizes of blisters have been found, and work is in progress to prevent the blister formation completely.

INTRODUCTION

For nearly twenty years the Laboratory has been interested in organic coating problems associated with the bulk storage of hydrocarbon fuels (1). Until the mid-1950's major interest was centered upon the need for better types of lining materials for large, underground concrete fuel-storage tanks, and slight attention was directed toward linings for steel tanks. However, in recent years the advantages of lining steel tanks have been recognized, and considerable effort has been made to develop such linings (2,3).

The environment within a large fuel-storage tank is particularly severe for organic coating materials. Since the tanks are almost always filled with some type of liquid, there is a constant tendency for the organic material to be penetrated and softened, or dissolved. Most organic linings are exposed to three different types of solvolytic attack—aliphatic hydrocarbons, aromatic hydrocarbons, and aqueous solutions. Since the linings are thin, are over a steel sub-surface which is subject to corrosion, and are expected to remain intact for long service periods, there are few types of organic coatings which are suitable for this application. Resistance to biological attack also is a requirement of linings of tanks in many areas.

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Fig. 1 - Blistering on the bottom of a polyurethane-lined tank

POLYURETHANE COATINGS FOR IMMERSSED STEEL

Because of their exceptional chemical resistance and toughness, it would appear that a definite place for polyurethanes should be found in tank lining applications (4-6). However, most large tanks collect some water, and in the bottom areas polyurethane linings have exhibited a persistent tendency to blister. Figure 1 shows

the bottom of such a tank, and the blistering which occurred during 9 months' service. On the wall areas which are exposed to fuels only, the polyurethane linings have remained in perfect condition for years and appear to be the easiest to clean of any materials used in this application.

Polyurethane coatings are more complex than most other types of lining materials because of the extensive and various reactions which occur as they form. Because of this, the problem of determining the exact mechanism by which blisters develop under the coatings is particularly difficult, and any of a number of physical or chemical circumstances could initiate the blister formation. Some variables suspected of having a role in the blistering of polyurethane tank linings have been investigated individually, and some peculiar anomalies have been discovered. For instance, polyurethanes generally require longer times for blister development in water at 130°F than at 75°F, and the blisters are larger in the cooler medium. Also, corrosion beneath unpigmented polyurethanes increases with increasing film thickness when the coatings are applied from ester-aromatic solvent systems, and decreases with increasing film thickness when the coatings are applied from nitrated solvents. The effects of different variables upon blistering and corrosion of steel-polyurethane systems are described in the following paragraphs.

IMMERSION CONDITIONS

A typical, pigmented polyurethane, produced from the adduct of toluene diisocyanate with trimethylolpropane and polyester, was applied to sandblasted, wash-primed steel panels. Identical panels were constantly immersed in tap water at two different temperatures for 26 weeks. In Table 1, and subsequently, the blisterings which occurred are compared by use of ASTM Photographic Reference Standard criteria (Fig. 2). Blister sizes are rated according to the numerical scale from 0 for complete film failure to No. 10 for no blistering. Blister densities are rated by abbreviations as follows: f. for few, m. for medium, m. d. for medium dense, and d. for dense. This immersion series was repeated several times with the consistent result that hot water was

TABLE 1
The Effect of Water Temperature Upon
Polyurethane Film Performance
In Immersion

Immersion Temperature (°F)	Immersion Time (weeks)	ASTM Blister Rating
75	26	No. 2-No. 6 m.
130	26	No. 10 (no blistering)

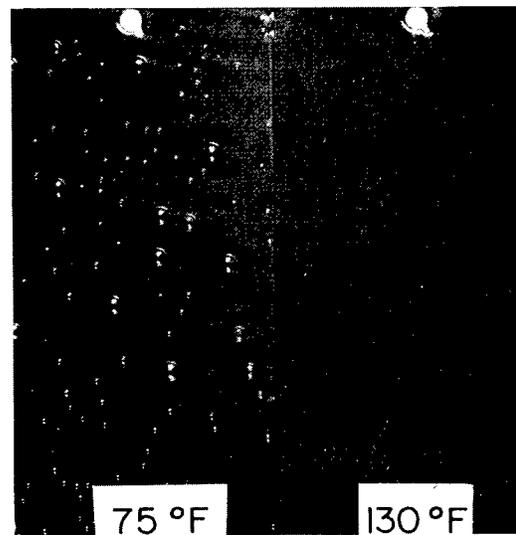


Fig. 2 - The effects of immersion temperature upon the performance of urethane coatings on steel

less detrimental to the coatings than water at room temperatures.

STEEL SURFACE PREPARATION

The nature of the metallic surface to which a polyurethane coating is applied has a considerable effect upon the immersion performance of the resultant system. Blistering of the coating and corrosion of the metallic surface may be varied between complete failure and long-term durability, as illustrated in Fig. 3. The panel in the upper left (a) exhibits slight corrosion of a cold-rolled steel surface of 30 to 50 μ in. roughness under an unpigmented polyurethane,

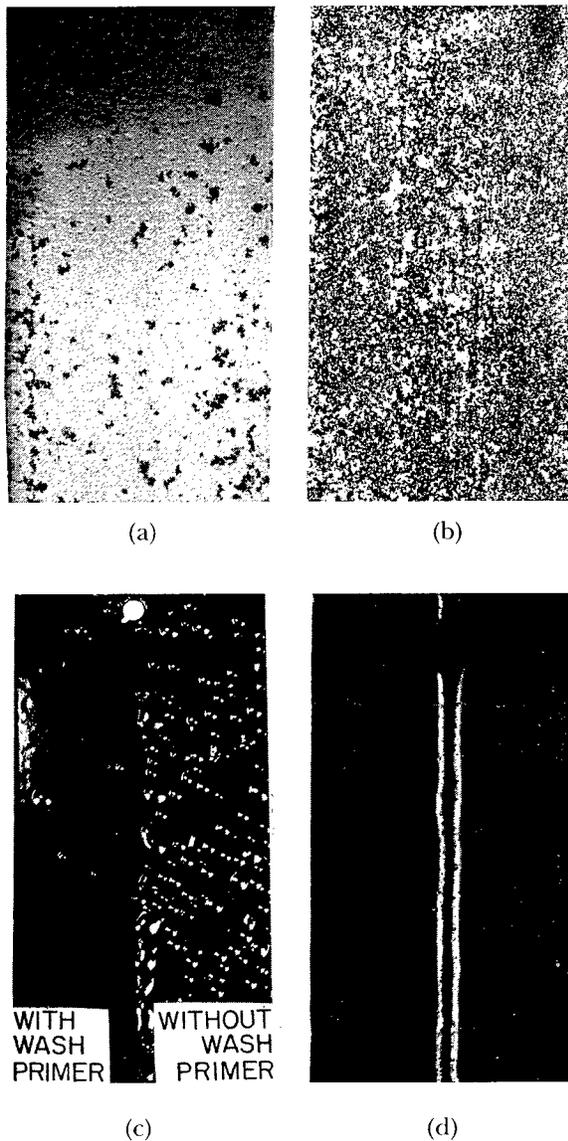


Fig. 3 - The effects of various steel surface preparations on immersion performances of urethane coatings; (a) Clear urethane on cold-rolled steel; (b) Clear urethane on lightly ground steel; (c) Pigmented urethane on sandblasted steel; (d) Pigmented urethane on aluminum metalized steel with center weld bead.

resulting from 3 month's immersion in water. The coating on the panel on the upper right (b) was identical, but the steel surface was given a 15 to 20 μ in. grind before the coating was applied. The difference in visible corrosion may be the result of the inherent resistances of the two types of steel surfaces; however, it is

apparent that the coating on the ground surface has allowed almost total corrosion of the substrate.

The panel in the lower left corner (c) was sandblasted over its entire surface, and the left half of the surface was treated with polyvinylbutyral-phosphoric acid wash primer (Mil-P-15328B). A pigmented polyurethane coating system was then applied, and the panel was immersed in water for 6 months. There is a clearly visible demarcation line between the halves of the panel surface. Whereas the polyurethane applied directly to sandblasted steel blistered extensively, there is only slight blistering over the wash-primed surface. A similar coating system was applied to the panel on the lower right (d). The surface was prepared for coating by spraying molten aluminum metal over sandblasted steel. This process provided a rough, granular surface which, unlike steel, was semi-noble. After 13 months' immersion in water, no impairment of the coating of any nature was in evidence, and it was apparently as sound as before immersion. Slight irregularities which are visible on the coating surface were present at the start.

SOLVENTS AND FILM THICKNESSES

Series of unpigmented polyurethanes were applied to steel panels with 15 to 20 μ in. ground surfaces. The hydroxyl component was polyester, and the NCO/OH ratio was 0.6/1 in all cases. Films were applied at two thicknesses from each of four solvent systems. In Fig. 4, the panels A, B, C, and D were coated at 1.0 ± 0.1 mil thicknesses, and the panels E, F, G, and H were coated at 1.6 ± 0.1 mil. The solvents from which the films were applied are shown in Table 2a. In Table 2b, the panels are rated according to the ASTM Photograph Reference Standards for blistering and for resistance to rusting (Type II rusting; rust with blisters). The evaluation was made after the series had been immersed in water at 75°F for 90 days. Rusting is rated from 0 for total failure to No. 10 for no rusting.

Several interesting observations can be made with respect to the coatings of this series. First, rusting of the steel beneath a coating was always accompanied by blistering of the coating; however,

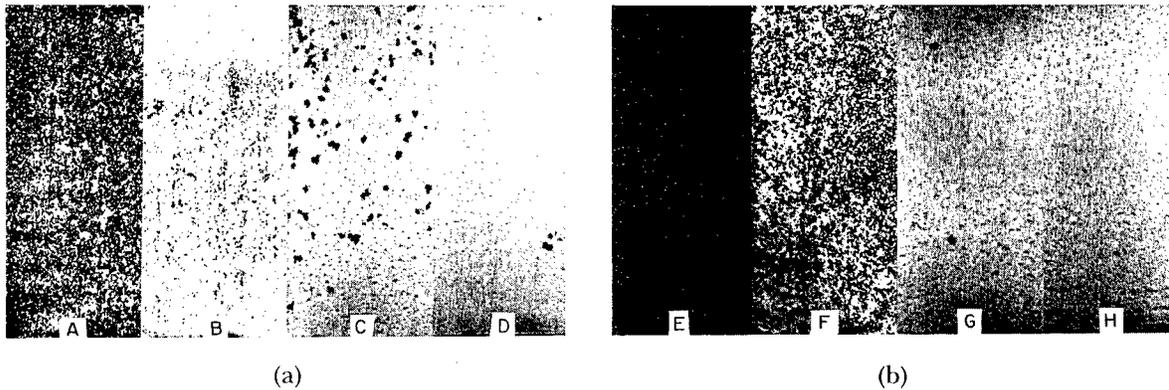


Fig. 4 - The effects of solvents and film thickness on immersion performance of unpigmented urethane coatings

TABLE 2a
Solvent Systems Used in Coating the Panels of Fig. 4
with Polyurethanes

Panels	Solvent (volume-percent)				
	Ethyl Acetate	Cellosolve Acetate	Butyl Acetate	Toluene	2-Nitropropane
A and E	25	25	25	25	—
B and F	—	13	62	25	—
C and G	25	25	—	25	25
D and H	13	12	—	—	75

TABLE 2b
The Effects of Solvents and Coating Thickness
Upon the Water-Immersion Performance of a
Polyurethane Coating

Panel Designation	Film Thickness (± 0.1 mil)	Blister Rating	Resistance-to-Rusting Rating
A	1.0	No. 8 m.d.	No. 2
B	1.0	No. 8 f.	No. 6
C	1.0	No. 6 m.	No. 6
D	1.0	No. 6 m.	No. 8
E	1.6	No. 8 d.	0
F	1.6	No. 8 m.d.	No. 3
G	1.6	No. 6 m.d.	No. 7
H	1.6	No. 6 m.d.	No. 10

blistering of the coating was not always accompanied by visible rusting. Evidence of this is clearly seen on panels D and H, on which the coatings are blistered, but very little rusting is visible. Second, as the thickness of the coating applied from ester-aromatic solvents increased, the amount of subsequent corrosion on the steel surface increased (compare panels A and E, B and F). However, the increase of thickness of the coatings applied from solvents containing 2-nitropropane caused a corresponding decrease in subsurface corrosion (compare panels C and G, D and H). Third, the substitution of 2-nitropropane for butyl acetate (volume for volume in the cellosolve acetate, ethyl acetate, and toluene system) caused a dramatic reduction in the extent of corrosion under the resulting coatings (compare panels A and C, E and G). This effect was not general, however, and also depended upon the nature of the polyester used to produce the polyurethane.

URETHANE PRIMER PIGMENTATION

A pigmented polyurethane system of the polyester-type was formulated with a set of differing primer pigments. The coatings over the primer were identical in all cases, and the systems were applied to sandblasted, wash-primed steel panels. The primers were formulated from corrosion-inhibitive pigments and extenders, except for the control, which contained no inhibitive pigment. The primers were polyester-type polyurethanes, formulated with a pigment volume of 35%, of which 60% was corrosion-inhibitive pigment and 40% was extender. Figure 5 shows the conditions of the coatings after 16 weeks' immersion in water, and the systems are identified and rated in Table 3.

One deduction which can be drawn from these data is that corrosion-inhibitive pigments of the chromate type are not optimum for the polyurethane coating. The blister concentrations on panels with zinc and strontium chromates were greater than those on the control panels. However, a definite reduction in blistering tendency resulted from the use of the basic lead silicochromate-barium metaborate pigment system. When the same system was applied

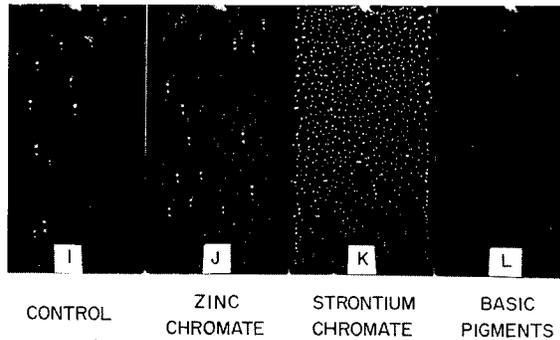


Fig. 5 - The effects of primer pigmentation upon urethane performance

to some cold-rolled steel panels, a few, relatively large blisters developed, and the liquid within the blisters was distinctly alkaline (pH= 8). When the tops of the blisters were removed, a small blemish of only about 1% of the total blister area was found near the central point of each, and each blister had developed in such a manner that the primer was laterally bisected. Part of the primer stayed on the steel, and part of it adhered to the covering coats. In some cases the blemish on the remaining primer was accompanied by corrosion of the steel immediately beneath it, and in other cases the metal was bright beneath the blemish.

ISOCYANATE-HYDROXYL RATIO OF THE PRIMER VEHICLE

A series of pigmented coatings of the polyester-urethane type were applied to sandblasted, wash-primed steel panels. The urethane primer coatings contained zinc chromate and were formulated so that the isocyanate/hydroxyl ratio increased from coating to coating. The covering coats were the same in all cases. In Table 4, the blister ratings are tabulated for the coatings after 16 weeks' immersion in water at 75°F.

At the 0.8 NCO/OH ratio, large blisters developed, under which there were usually small areas of steel corrosion. At the 1.0 ratio, there were fewer blisters of more uniform sizes. As the ratio exceeded the stoichiometric value, the blisters became varied in size with a high concentration of small blisters, scattered among fewer large ones. Under these blisters, the steel surface areas were extensively corroded.

TABLE 3
The Effects of Urethane Primer Pigmentation
upon Water Immersion Performance

Panel Designation	Primer Pigmentation	Blister Rating (16 weeks' immersion)
I (control)	Titanium dioxide, iron oxide, talc, mica	No. 8 and 2, f.
J	Zinc chromate-talc	No. 6 and 2, m.
K	Strontium chromate, iron oxide, talc, mica	No. 4, d.
L	Basic lead silicochromate-barium metaborate-iron oxide-mica	No. 10

TABLE 4
The Effects of the Primer Vehicle
Isocyanate/Hydroxyl Ratio Upon Water
Immersion Performance

NCO/OH	Blister Rating (16 weeks' immersion; water temperature 75°F)
0.8	2-6, m.
1.0	4, f. to m.
1.1	4-8, f. to m; 9, d.
1.2	3-7, m; 9, d.

STRUCTURE AND FUNCTIONALITY OF THE HYDROXYL COMPONENT

Panels were prepared with unpigmented polyurethane coatings of the two most prevalent types—polyester and castor oil. Two series of each type hydroxyl component were prepared using the toluene diisocyanate-trimethylolpropane adduct, and the NCO/OH ratio was 1/1 in all cases. Of each hydroxyl type, a polyurethane of higher functionality and one of lower functionality were produced. Coatings 1.0 mil thick were applied to ground steel panels, and the panels were immersed in water at 75°F for 6 months before evaluation. The panels are illustrated in Fig. 6 and described in Table 5.

Two results are most outstanding with respect to this series. First, regardless of the hydroxyl component, better protection for the steel was provided by the material of lower functionality. This is particularly evident in the polyester series

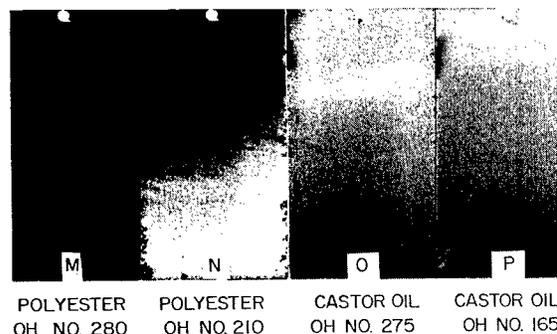


Fig. 6 - The effect of hydroxyl component structure and functionality upon polyurethane immersion performance

and can be clearly seen by comparison of panels M and N of Fig. 6. Second, the coatings prepared from castor oil provided better steel protection than those prepared from the polyesters. A comparison of panels N and O reveals that the castor oil coating of OH number 275 was at least equivalent to the polyester coating of OH number 210. The coating on panel P, prepared from specially dried castor oil of low functionality, exhibited the best overall performance of any urethane which has completed a full 6 months' immersion.

SUMMARY OF EXPERIMENTAL OBSERVATIONS

When a polyurethane coating is applied to steel and the resulting system is immersed in water, there is a persistent tendency for blisters to form within the coating. Generally the blisters are tough, liquid-filled hemispheres which are

TABLE 5
The Effects of Hydroxyl Compound Structure and Functionality Upon
Immersion Performance of Polyurethane Coatings

Panel Designation	Type OH Component	Blister Rating	Rust Resistance Rating
M	polyester; OH Number 280	No. 4, d.	No. 1
N	polyester; OH Number 210	No. 9, m.d.	No. 8
O	castor oil; OH number 275	No. 9, m.d.	No. 8
P	castor oil (very dry); OH number 165	No. 8, f.	No. 10

liberally scattered at individual sites over the coating. Any of a number of variables will affect blister densities, blister sizes, and/or the extents of steel rusting under the films.

THEORY AND DISCUSSION

Since polyurethane coatings on steel have exhibited such a persistent tendency to blister in water immersion, it would appear that there is some inherent characteristic to be overcome if the blistering is to be avoided. Two possibilities are suggested which take into account basic urethane characteristics and may account for the blistering phenomena.

1. There are minute entrapments of carbon dioxide within polyurethane films. Since carbon dioxide is a soluble gas which produces a weakly acidic solution, a very tiny entrapment near the steel surface should produce a "weak" site within a polyurethane coating. As water permeates a film and dissolves the gas within an entrapment, a situation of corrosive and osmotic potential develops.

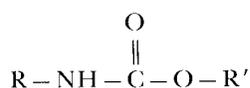
Several observations from the data presented may be rationalized with the assumption of blister-initiation sites filled with carbon dioxide. The relative resistance to blistering of coatings in hot water may result from a softening of the films and outward diffusion of entrapped carbon dioxide. Inherent corrosion resistivities of various steel surfaces to attack by weakly acidic solutions may explain the different blister tendencies in the surface studies, since the wash-primed and metallized surfaces were particularly resistant. Increased steel corrosion under thicker films applied from ester-aromatic solvents may

reflect poor solvent and carbon dioxide release. Decreased steel corrosion under thicker films from nitrated solvents may result from good solvent and carbon dioxide release, combined with the improved protection of a more coherent film (7). Basic primer pigments, which shield the steel surface with an alkaline layer, probably "scavenge" carbon dioxide. In addition to the neutralization of any carbonic acid by the alkaline medium, the lead and barium present in the moist primer should keep the carbonate ion concentration at a low level. This action may explain the superior performance of basic lead silicochromate-barium metaborate relative to the inhibiting pigments and the inert control pigments. The relatively poor performance of the slightly soluble inhibiting pigments probably resulted from their increased osmotic potentials. As the isocyanate/hydroxyl ratio exceeded 1/1, the blister density increased, and the probability that carbon dioxide was entrapped in the film also increased, since the excess isocyanate had to dissipate by a carbon dioxide-producing reaction. Polyester components of lower functionality required less isocyanate for crosslinking than those of higher functionality, and consequently, the potential for carbon dioxide entrapment was lower at any NCO/OH ratio of 1/1 or lower. Finally, the dry, lower-functional castor oil produced a blister-resistant film. In this case, the carbon dioxide-producing side reactions should have occurred to a minimal extent.

The nature of the under-blister areas of pigmented polyurethane films may also be cited in support of the carbon dioxide entrapment theory. A blister is frequently an area of inter-

coat delamination, with the primer intact, which contains a more-or-less-central blemish. This blemish most probably occurs as a result of chemical action, and the steel substrate beneath it is not always rusted. The most likely chemical "hot spot" within a urethane coating should be a carbon dioxide-filled bubble. Such a site probably initiates the blister, feeds reaction processes including corrosion, and helps initiate osmotic growth of blister diameters.

2. The urethane group is basically hydrophilic. In a sense it is an ester-amide, and as such, constitutes a center of electrical polarity. Most coatings are produced containing *N*-substituted carbamate esters of the following type:



where R is aromatic when a toluene diisocyanate derivative is employed, and R' is nearly always aliphatic. In Table 6 some solubilities in water at 15.5°C are compared for various simple urethanes.

TABLE 6
Solubilities in Water of Various Urethanes (8)

N-Substituent (R)	O-Substituent (R')	Sol. in Water (g /100 ml at 15.5°C)
Methyl	Ethyl	94.7
Ethyl	Ethyl	63.2
Propyl	Ethyl	9.8
Phenyl	Ethyl	very slightly soluble

Although the urethane group cannot carry the *N*-phenyl group into water solution, it obviously has a pronounced tendency to do so. It is probable that the better water immersion performance of urethane coatings of lower functionality results in part from the decreased concentration of urethane linkages within the films.

The radial growth of a blister, after initiation, is certainly a diffusion process and is probably a straightforward osmosis. The blisters are filled with water under pressure, and frequently they arise out of a film that adheres tightly around the periphery. Corrosion-inhibiting primers, such as zinc chromate, produce solutions within

the blisters, and the liquid removed from such a blister is distinctly colored. This, of course, promotes osmosis.

In summary, it is believed that urethane coatings have an inherent affinity for water, that they are fair membranes for osmosis, that they contain blister-initiation sites which are probably small bubbles of carbon dioxide, and that radial blister growth occurs by an osmotic process after initiation.

SUMMARY

The first urethane tank linings of the polyester type to be installed in shore facilities of the Navy were placed into service in 1959. In spite of some blistering in the bottom areas, the linings have remained serviceable, and maintenance personnel have expressed satisfaction with overall performance. The blisters are tough and resist rupture. Under most of them, corrosion of the steel substrate is of little consequence and the corrosion products do not escape to pose a fuel-contamination problem. However, this defect in such a promising type of tank lining material should be eliminated. The solution of this problem is the subject of continuing research, and at present work is in progress, based upon the knowledge and theories expressed, to formulate coatings which will prevent, or greatly reduce, the blister formation. The outcome of these experiments will be described in future reports.

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