

# Laboratory and Human Exposure Evaluation of Unique Sunscreen Formulations

A. F. STEINHAUER, Ph.D\*

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**Synopsis**—A screening test was developed for efficacy of SUNSCREEN FORMULATIONS which was based on ULTRAVIOLET analysis of alcohol extracts taken from skin treated with sunscreen. This type of analysis showed the superior retention of some unique sunscreen formulations in tests where the subject's forearms were subjected to water sprays and also in swimming tests wherein the formulation was applied to grid areas on the back. These formulations were unique in having minor amounts of an ACRYLATE POLYMER present. Dried films of these formulations were examined under a SCANNING ELECTRON MICROSCOPE and showed a coherent film having a multiplicity of voids. The sunscreen oil had been entrapped in these spaces before the high vacuum of the instrument caused its volatilization.

Field evaluations of suntan and sunblock formulations containing polymer showed excellent sunscreen retention under severe challenge conditions including 45-minute swims and sauna baths followed by sun exposure.

## INTRODUCTION

Much has been said and written about the problem of sunburn. As sunworshipping has become more and more widespread, the need for efficacious suntan lotions has become more acute. Kligman (1) and other dermatologists have pointed to the aging effects on human skin and the possibilities of skin cancer developing from overexposure to the sun's rays.

Numerous sunscreen preparations have been marketed to prevent this damage from sunlight. But so many of these are easily removed as a result of sweating or by immersion in water (2). The need for more retentive sunscreen preparations was the stimulus that brought about our investigation of possible new vehicles for common approved sunscreen chemicals.

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\*Dow Chemical Co., 2020 Dow Center, Midland, Mich.

Since the evaluation of sunscreen preparations is quite difficult, it was necessary to apply several new evaluation techniques both in the laboratory and in the field to determine the efficacy of the formulations discussed in this paper. Because of a long history of use, several commercial sunscreen products were used to assess the comparative performance of the experimental products.

#### EXPERIMENTAL AND RESULTS

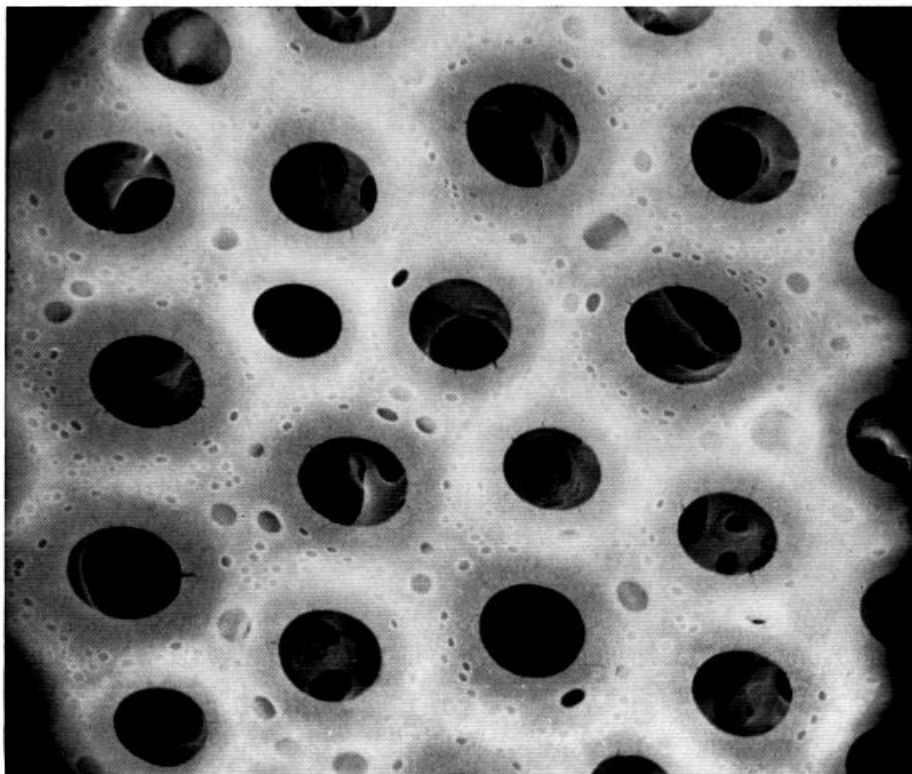
During the course of an investigation involving the use of acrylate polymers in certain formulations containing rather large amounts of oil, an unusual structure was observed in the dried films. It consisted of a polymer matrix surrounding small droplets of oil. This suggested the possibility of using such formulations to help retain sunscreen oils on the skin. It was found that the entire system had to be in proper balance, but then amounts of sunscreen oil as large as 20X the weight of polymer could be more effectively retained on the skin. Unfortunately, the composition of these sunscreen formulations cannot be discussed because of secrecy requirements. But this should not be too much of a handicap to the reader if he remembers that this paper is intended primarily to include evaluation techniques. It can be stated that the sunscreens used in these formulations included homomenthyl salicylate (HMS) and amyl-*p*-dimethylaminobenzoate.

The scanning electron microscope has been a very useful tool in establishing the structure of these films. In Fig. 1, we see a photograph (7750X) of a film made from a formulation containing the acrylate polymer and sunscreen agents. Here the polymer has formed a coherent film having a multiplicity of voids in which the sunscreen oil has been trapped. Due to the high vacuum of the electron microscope all of the oil has volatilized and we simply see the voids where it has been. Closer examination of the larger holes show similar holes below the surface which do overlap to give continuity to the ultraviolet protection. This film can be sliced to give a more open structure as seen in Fig. 2. The integrity of the individual cells has now been broken.

Large amounts of sunscreen can be retained in this layer in such a way that it is not prevented from functioning in its normal manner. Thus, the film serves to prevent loss of the sunscreen by volatilization or by washing away or by absorption into the skin. Frequently the sunscreens might normally impart an oily or greasy feel when applied without the film former; but this greasy feel is not found or at least is greatly diminished when the polymer is utilized.

#### *Spot-Burn Tests*

The structure of these films containing the acrylate polymer suggested that the sunscreen should remain on the skin longer. Also, this type of sunscreen formulation should give an umbrella effect wherein the active sunscreen is



*Figure 1.* Scanning electron micrograph of dry film prepared from formulation containing acrylate polymer and sunscreen (X7750)

held slightly above the skin's surface. It is our opinion that this type of protection is superior to that provided by formulations in which the sunscreen sinks into the skin and the outer surfaces are no longer protected.

Some of our early evaluations of these formulations were made on subjects who were showered under standardized conditions after application of lotions and then were exposed to uv lamps to determine burn resistance of treated areas.

Three different lotions were applied to the right, center, and left backs. Approximately 0.3 ml of lotion was applied to 16 in.<sup>2</sup> of skin. This area of the body was then placed under a shower with a wide spray head for 10 min. After air drying, the subject's back was exposed to a commercial uv lamp for approximately 15 min. The back had first been covered with a piece of fabric, sections of which were cut out to permit the lamp's rays to penetrate. Photographs of the back with its small burned spots were then taken 6 hours later.

The degree of sunburn was rated by two observers examining the photographs of 15 subjects exposed to this treatment and redness was rated on a

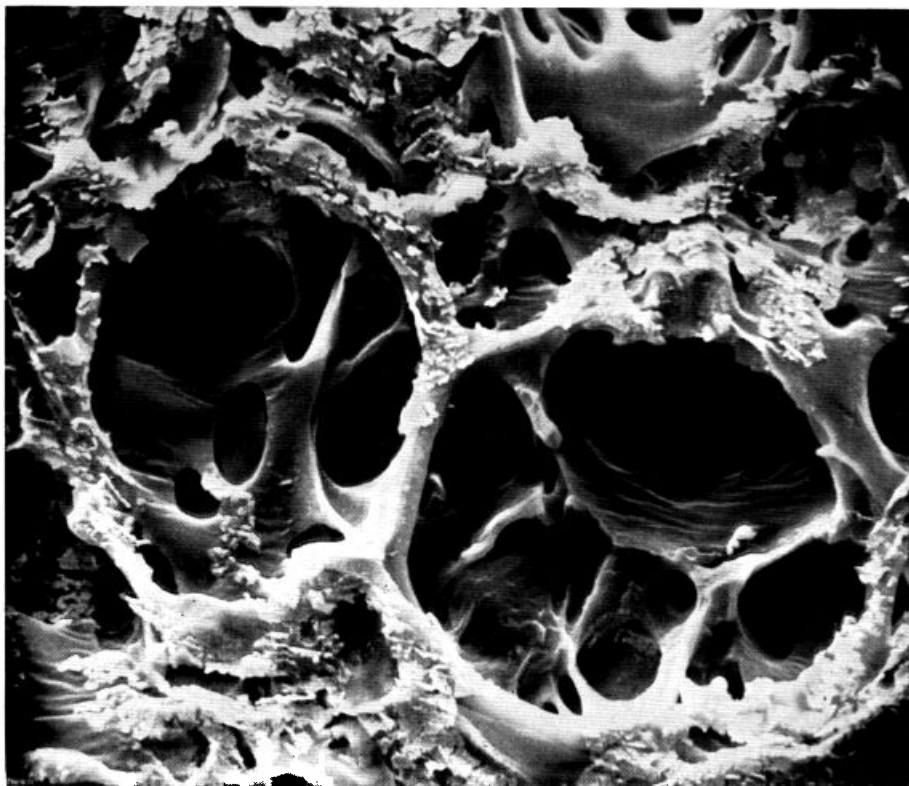


Figure 2. Scanning electron micrograph of sliced film shown in Fig. 1 (X7750)

scale of 1 to 5, with 5 corresponding to extreme redness. The experimental formulation containing acrylate polymer will be called Formulation 1 and a commercial lotion containing homomenthyl salicylate will be called Commercial Suntan Lotion A. The average redness ratings obtained from these spot-burn tests are given in Table I and show the superior performance of Formulation 1.

Table I  
Results of Spot-Burn Tests

Product	Average Redness Rating
Formulation 1	1.3
Formulation 1 (no polymer)	2.7
Commercial Suntan Lotion A	2.9

*Spectrophotometric Analysis*

The above evaluations are subjective but the improvement noted with Formulation 1 is substantial and real. However, a more quantitative measure was needed of how well sunscreens are retained on the skin. For this purpose, a screening test was developed for efficacy of sunscreen formulations which was based on uv analysis of alcohol extracts taken from skin treated with sunscreen. A constant amount of suntan lotion was spread over a constant area of skin—the anterior forearm was often used, but it was also possible to run the test on the back or leg. A bottle containing a set volume of alcoholic solvent was inverted onto the treated surface and carefully shaken for a given period of time. This action would extract all of the alcohol-soluble material within the inner area of the bottle's mouth. The sample was then analyzed in a Beckman DU spectrophotometer to determine the absorption peak at 305  $m\mu$  which is in the spectral area of maximum burning from the sun's rays.

For some of our laboratory testing, subject's arms were sprayed 20 min with water after suntan formulation had been applied. A spray head similar to those used in garden sprinkle cans was attached to the water faucet. It measured 3.25 in. in diameter and contained 56 holes of 0.03-in. diameter. Water at 78-80°F. was forced through this head at a rate of 2.5 gal/min. The arms were placed approximately 10 in. from the spray head. Alcohol extractions were performed before and after this stress situation. Typical performance of the polymer formulation is shown in Table II. In this test, 0.3 ml of lotion was spread on 16 in.<sup>2</sup> of arm surface. The change in the uv absorption values can be directly translated into per cent loss of sunscreen from the skin, which in the case of the polymer formulation is 33% as contrasted with 85% for the commercial product. An even greater loss (93%) was found in a formulation similar to Formulation 1 but with no polymer present.

Table II  
Arm Spray With Ultraviolet Analysis of Alcohol Extracts

Product	Absorption		
	Before	After	% Loss
Formulation 1	0.63	0.42	33
Commercial Suntan Lotion A	0.53	0.08	85
Formulation 1 (no polymer)	0.367	0.025	93

To show the reliability of this test the absorption values representing the average of three extractions before and three extractions after the arm spray test on ten individuals are listed in Table III. Half of the group applied 0.2 ml of Formulation 1 and the other half applied 0.2 ml of Commercial Lotion A to 16 in.<sup>2</sup> of arm surface. Note that this is less lotion than used on the subjects in Table II.

Table III  
Arm Spray—Ultraviolet Analysis of Alcohol Extracts

	Absorption		
	Before	After	% Loss
Subjects 1–5, Formulation 1	0.27	0.18	33.3
	0.27	0.19	29.6
	0.22	0.15	31.8
	0.28	0.17	39.3
	0.27	0.21	25.0
Average	0.264	0.180	31.8
Subjects 6–10, Commercial Suntan Lotion A	0.28	0.02	92.8
	0.28	0.01	96.4
	0.27	0.04	85.2
	0.37	0.03	91.9
	0.25	0.03	88.0
Average	0.290	0.026	91.0

The alcohol extraction procedure was also used to evaluate sunscreen performance during actual swimming tests. Here, given amounts of suntan lotions were applied to grid areas on the back and extractions were made before and after swimming for 45 min. In Table IV is shown a typical performance of the polymer formulation compared to two commercial products. It is apparent that sufficient sunscreen is retained on subjects treated with Formulation 1 to protect them against the sun's rays even after swimming for 45 min. The commercial products give insufficient protection after this much water challenge. As stated earlier, Lotion A contains homomenthyl salicylate, the same sunscreen as contained in Formulation 1. On the other hand, Lotion B contains glyceryl *p*-aminobenzoate and appears to be somewhat more sensitive to water challenge than Lotion A.

Table IV  
Forty-five Minute Swim with Ultraviolet Analysis of Alcohol Extracts

Product	Absorption		
	Before	After	% Loss
Formulation 1	0.52	0.30	42
Commercial Suntan Lotion A	0.58	0.15	75
Commercial Suntan Lotion B	0.57	0.08	86

#### *Fluorescent Tracer Evaluation*

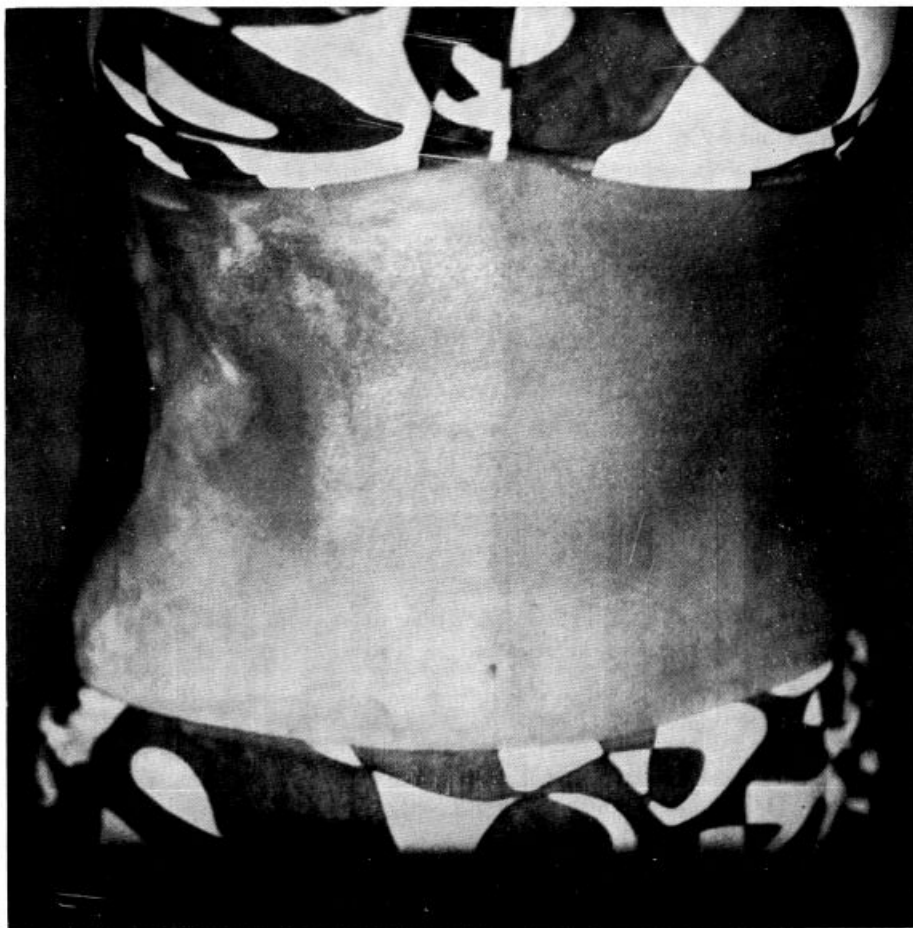
Another evaluation technique that was used to study the loss of suntan lotion under stress situations involved the use of an optical brightener called Tinopal SFG.\* A very small amount (0.025%) of this dye was added to commercial suntan lotions and to the lotions containing acrylate polymer. In a

\*Geigy Industrial Chemicals, Ardsley, N.Y.

dark room in the presence of ultraviolet light this fluoresces and serves as a tracer to establish how much lotion is present on a given area of the body. Then by using a Polaroid camera equipped with a uv filter it is possible to take photographs of the fluorescent areas and thus record the distribution and retention of suntan lotion.

One thing learned during these tracer tests was that there is considerable variation in how much suntan lotion individuals apply to their skin. Also, they do not always apply it evenly.

During comparisons of suntan lotions the fluorescent tracer evaluation can show up gross differences. In Fig. 3 is seen a subject whose photograph was taken under uv light after sunning and turning every 20 min for a period of 3 hours. On her right side she had applied Formulation 1 and on her left side



*Figure 3.* Removal of suntan formulations by abrasion; fluorescent areas show presence of sunscreen. Left side, Lotion A; right side, Formulation 1.

she had applied Commercial Lotion A. The commercial lotion has been removed by perspiration and abrasion whereas the polymer lotion system appears intact.

#### *Field Evaluations of Suntan Formulations*

There are many variables involving use by different consumers: different complexion types, different tendencies in amounts applied, variations in evenness and completeness of application, etc. To study the performance of polymer formulations under field conditions a group of 49 Miami housewives was recruited for several days of controlled tests. They participated in different phases of the study: (a) normal usage patterns, (b) fresh water challenge, (c) salt water challenge, and (d) tanning with and without abrasion.

Some of the evaluation tests which were described previously were found valuable in assessing the performance of the suntan products under field conditions. The alcohol extraction test was used to determine retention of sunscreens under the above type of challenge and also to gauge how much and where a normal consumer applies lotion. Additional information pertaining to usage patterns and retention was obtained by the fluorescent tracer evaluation technique. Following initial application, all subjects were checked in the dark room to ascertain spreadability and uniformity of application with each product, and to insure that all subjects were adequately protected prior to sun exposure.

The polymer formulation performed well when compared with Commercial Lotion A. Its improved resistance to water challenge was established and certain aesthetic advantages were seen including reduced greasiness, ease of application, and no sand pick-up. It was observed that consumers tended to apply discontinuous coats of lotion with both Formulation 1 and Commercial Lotion A. Subjects sometimes failed to protect large areas of the body such as entire arms or legs, as revealed by visual inspection of coverage under ultraviolet light.

There was abrasion of suntan lotions observed for all products upon contact with terrycloth towels and beach mats. There were indications that the polymer formulation was more resistant to abrasion.

#### *Sunblock Formulation*

Formulation 1 was designed as a suntan formulation. An increase in sunscreen level produced a very effective sunblock type of product (Formulation 2). Again HMS and amyl-*p*-dimethylaminobenzoate were the sunscreen agents. Screening tests demonstrated that it was retained much better than two leading commercial sunblock products as shown in Table V. Our standard 20-min arm spray test was used to obtain these data. Sunblock A contained isoamyl-*p*-dimethylaminobenzoate and Sunblock B contained 2-hydroxy-4-methoxy-benzophenone-5-sulfonic acid.

Table V  
Arm Spray—Ultraviolet Analysis of Sunblock Products

Product	Absorption		
	Before	After	% Loss
Formulation 2	0.75	0.41	45
Commercial Sunblock A	0.62	0.06	90
Commercial Sunblock B	0.79	0.05	94

Field testing of our sunblock, Formulation 2, was conducted at Concord, Calif., under conditions of intense ultraviolet exposure. Three challenge conditions were used: long-term sun exposure with no external insult, water insult with sun exposure, and perspiration insult with sun exposure. Commercial Sunblocks A and B were used for comparison in all three test conditions. A total of 61 male and female subjects participated in this test. Two products were applied to each subject in a half-body type test. After challenge the subjects were exposed to 2–4 hours of midday sun and color evaluation was made after 5 hours by three observers. Photographs of each subject were also taken.

The color development was rated on the following scale: 0, no color development; 1, slight color; 2, medium color; 3, intense color. Table VI shows that with 4-hour sun exposure there has been more color development in the case of Sunblock A than with Formulation 2.

Table VI  
Sun Exposure (4 Hours)—No Insult

Product	No. Subjects	Ave. Color
Formulation 2	8	1.3
Commercial Sunblock A	8	2.0
Formulation 2	8	1.6
Commercial Sunblock B	8	1.8

An exposure to 45 min of swimming and 2½ hours of sun resulted in marked differences of color development between Formulation 2 and the commercial sunblocks (Table VII). The effects of a 20-min sauna with its resultant perspiration challenge is shown in Table VIII. Again, the improvement due to Formulation 2 is demonstrated although the challenge does not seem to be as severe as the swimming tests.

Table VII  
Water Insult (¾ Hour)—Sun Exposure (2½ Hours)

Product	No. Subjects	Ave. Color
Formulation 2	9	1.3
Commercial Sunblock A	9	2.5
Formulation 2	20	1.2
Commercial Sunblock B	20	2.6

Table VIII  
Perspiration Insult ( $\frac{1}{3}$  Hour)—Sun Exposure (3 Hours)

Product	No. Subjects	Ave. Color
Formulation 2	8	1.0
Commercial Sunblock A	8	1.8
Formulation 2	8	1.2
Commercial Sunblock B	8	1.9

### SUMMARY

The scanning electron microscope showed a unique sponge-like structure of polymeric films containing sunscreens. This structure explained the improved sunscreen retention on the skin as well as the reduction of oily feel of these materials. The entire system had to be in proper balance with appropriate ingredients and a unique polymer.

Several evaluation techniques were used to determine the efficacy of those polymer formulations. These included rather standard spot-burning methods, spectrophotometric analysis of alcohol extracts of the skin, fluorescent tracer techniques showing distribution and retention of sunscreen, standard photographic methods, and visual inspection.

The sunscreen retention was followed by means of the above tests in laboratory water spray procedures, 45-min swims, and sauna baths with sun exposure. Polymer formulations showed superior sunscreen retention over commercial products in both laboratory and field tests. Certain aesthetic advantages also were noted such as nongreasiness, ease of application, and no sand pick-up.

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