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RESEARCH PAPER

Stability of UV Filters in Different Vehicles: Solvents and Emulsions

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ABSTRACT

In this paper, we analyzed the stability of several ultraviolet (UV) filters exposed to simulated solar light. Evaluation of the photostability of UV-A/UV-B filters has an important impact on the efficiency of sunscreen preparations. The purpose of this study is first to relate some of the solvent shifts that can interact with UV filters; secondly, it is to formulate sunscreen emulsions (oil in water and water in oil) in order to evaluate the photostability of sunscreens in the mixture, and therefore their efficiency in solar protection, because photostability and protection are closely linked together.

INTRODUCTION

Sunscreen formulations were conceived to protect the skin against sunlight damages, in particular, erythema, various skin lesions, and premature aging of the skin. These preparations were designed to absorb the ultraviolet (UV) radiations: UV-B and/or UV-A. Sunscreen formulations must be efficient and stable; thus, photostability of the sunscreen is an important aspect since sunscreen can interact with solvents and components of formulations and could reduce their efficacy. Furthermore, it has been shown that sunscreens will undergo degradation as a result of being exposed to UV light (1,2).

The aim of this work is to evaluate the stability of various sunscreen agents incorporated into different solvents and oil in water (O/W) and water in oil (W/O) emulsion formulations (realized with a significant percent of a mixture of studied solvent). For sunscreens, O/W and W/O emulsions are the most popular vehicles and will be formulations of choice for some time to come (3). W/O emulsions are usually used to realize waterproof formulation. Solvents used are three oils with a slight ability to penetrate the horny layer (4,5) and a

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polar solvent. In this study, we have eliminated all vehicles such as ethanol, which cannot be utilized in solar preparations. For most skin care formulations, emulsions are based on a mixture of different oils. In our case, the oil content contains paraffin liquid for its stability, low cost, and function as a moisture barrier. Coconut oil is employed for its high compatibility with the skin. Isopropyl myristate leaves no sticky or greasy feeling after application. In water phase, propylene glycol is used for some combined properties such as its ability to attract moisture, retard evaporation, and its moderately adhesive effect.

Four insoluble (in water) sunscreens have been chosen, according to the more frequently used in this field (6,7): two of them are UV-A absorbers (oxybenzone, padimate O) and the other two, are UV-B absorbers (octyl methoxycinnamate, avobenzone). The last filter studied is a water-soluble and UV-A absorber (sulisobenzone). The regulatory situation in the world is not harmonized and we give the regulation of sunscreens tested in the European Community (ECC) and in the United States: In the EEC cosmetic directive listing of UV filters in annex VII, we find in part I, the fully permitted list [oxybenzone (colipa number S38)] and in part II, the provisional list [padimate O (S8), sulisobenzone (S40), avobenzone (S66), octyl methoxycinnamate (S28)] (8). As for the U.S. Food and Drug Administration (FDA), sunscreens are categorized as drug products. Sunscreen ingredients not included in the monograph are considered new drugs and cannot be marketed without FDA approval (9). Only avobenzone is not listed as a sunscreen ingredient in category I (10).

MATERIALS AND METHODS

Materials

The 5 UV absorbers evaluated are reported in Table 1. The reagents used for dilution are hexane (Prolabo) and ethanol (95% v/v). The chosen vehicles are paraffin liquid (Primol®, Esso), coconut oil (Laboratory CPF, Melun), isopropyl myristate (Henkel), and propylene glycol (Prolabo). Three nonionic surfactants used are polyoxyethylen-20-sorbitan monostearate (Emulgin SMS20®, Henkel) and sorbitan monostearate (Dehymul SMS®, Henkel) to produce O/W emulsions, and methoxy PEG-22/dodecyl glycol copolymer (Elfacos E200®, Akzo) to produce W/O emulsions. Dimethicone (Silbione oil 70047®, Rhône Poulenc), carbomer (Carbopol 934®, Goodrich), cetyl stearyl alcohol (Lanette O®, Henkel), squalene (Sophim), and a preservative (Kathon CG®, Rhom and Haas) are used as additives. Distilled water is used for all emulsion formulations.

Instruments

Analyses of UV absorbers were performed on spectrophotometer UVIKON 922 (Kontron Instrument). The solar simulator used for irradiation was a xenon type (Proeclair S.A.) equipped with UV-visible lamp (Philips lamp SX 450 W). The distance source/object was 114 cm. Emulsions were prepared with a homogenizer Turbotest 33/300 (Rayneri).

Methods

Solvents Used for This Study

Table 2 lists the different sunscreens incorporated in solvents. Four solvents commonly used in emulsion formulations were chosen for this study and sunscreens were incorporated in these solvents at 1.3–2% levels. A bar magnet facilitated agitation (10 min) and the mixture was maintained at 20° ± 1°C for paraffin liquid, propylene glycol, and isopropyl myristate, and 35° ± 1°C for coconut oil (which is not liquid at 20°C).

Preparation of Oil/Water (O/W) and Water/Oil (W/O) Emulsions

Emulsions are prepared according to previous works (11–13) and the complete list of ingredients is reported in Table 3 (21% of emulsions correspond to the previously studied solvents). The water phase (Phase B) and the oily phase (Phase A and surfactants) are heated separately to 65°C. The aqueous phase is then added to the oily phase over 30 sec, and mixed by a homogenizer (Turbotest 33/300, Rayneri) at 400 rpm with progressive cooling for 45 min of homogenization at room temperature (25°C). About 300 g of emulsion was prepared for each test. No fragrances have been added since they can break down the formulation and give photosensitized reactions.

All emulsions realized are stable, and are suitable dermatological preparations or skin care products. They are currently available in the marketplace.

Table 1

Sunscreens Used in This Work

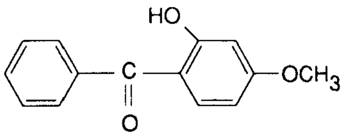
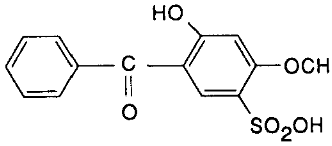
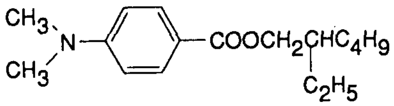
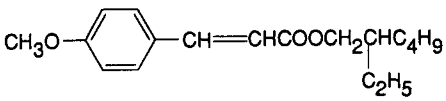
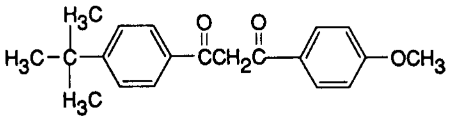
Alternative Names	Chemical Names	Origin	Formulary
Oxybenzone = benzophenone-3	2-Hydroxy-4-methoxy benzophenone	Sigma	
Sulisobenzone = benzophenone-4	2-Hydroxy-4-methoxy benzophenone-5-sulfonic acid	Sigma	
Octyl dimethyl PABA = padimate O	2-Ethylhexyl *p*-aminobenzoate	Escalol 507 Van Dyk	
Octyl methoxycinnamate	2-Ethylhexyl *p*-methoxycinnamate	Parsol MCX Givaudan-Roure	
Butyl methoxy-dibenzoylmethane = avobenzone	1-(4-*ter*-Butylphenyl)-3-(4-methoxy phenyl) propane-1,3-dione	Parsol 1789 Givaudan-Roure	

Table 2

Sunscreen Concentrations Used in Vehicles

	Sunscreens				
olvents	Oxybenzone	Sulisobenzone	Padimate O	Octyl Methoxy Cinnamate	Avobenzone
araffin liquid	2% (20 ± 1°C)	NS	1.5% (20 ± 1°C)	1.3% (20 ± 1°C)	NS
ropylene glycol	1.3% (20 ± 1°C)	1.3% (20 ± 1°C)	NS	1.3% (20 ± 1°C)	NS
oconut oil	1.4% (35 ± 1°C)	NS	1.4% (35 ± 1°C)	1.4% (35 ± 1°C)	NS
sopropyl myristate	1.5% (20 ± 1°C)	NS	1.5% (20 ± 1°C)	1.5% (20 ± 1°C)	1.5% (20 ± 1°C
)/W emulsion	2%	1.5%	1.4%	1.5%	NS
V/O emulsion	2%	1.5%	1.5%	1.7%	NS

IS = not soluble in these conditions.

Table 3

Emulsion Compositions

Emulsions	O/W	W/O
Phase A	Paraffin liquid 5%	Paraffin liquid 5%
	Isopropyl myristate 6%	Isopropyl myristate 6%
	Coconut oil 8%	Coconut oil 8%
	Dimethicone 0.5%	Dimethicone 0.5%
	Squalene 1.5%	Squalene 1.5%
	Lanette O 2%	
Surfactants	Emulgin SMS20 2.5%	Elfacos E200 15%
	Dehymuls SMS 2.5%	
Phase B	Propylene glycol 4%	Propylene glycol 4%
	Carbopol 934 P	
	Kathon CG 0.1%	Kathon CG 0.1%
	Water qs 100%	Water qs 100%

Sample Preparation and Spectrophotometric Determination

The ultraviolet spectrum for each sunscreen in hexane/ethanol mixture (1/2, v/v) is reported in Fig. 1. An analysis of variance on data allowed a linear regression between optical density (OD) and concentration of each sunscreen to be calculated. The regression formula appears as $y = bx + a$, where y is the OD, x is mg · liter^{-1} of sunscreen, b is the slope, and a is the intercept. We checked the linearity of each UV response (summarized in Table 4).

In each case (solvent or emulsion), a sample of 300 mg was laid in a watch-glass and irradiated by a solar simulator. Samples were exposed, respectively, to 0, 30, 60, 120, and 240 min. Then each analysis was performed in triplicate, and samples were diluted as required in hexane/ethanol (1/2, v/v); other solvents could increase or decrease absorbance (14).

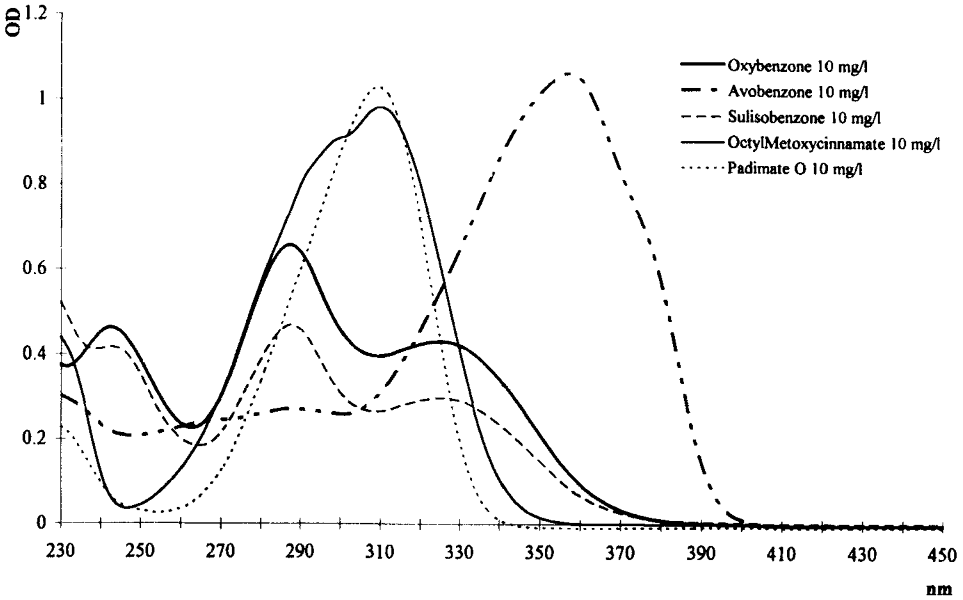


Figure 1. Sunscreen Ultraviolet spectra (hexane/ethanol mixture, 1/2 v/v).

Table 4

Linearity of UV Response for Sunscreens (Hexane/ETOH:1/2, v/v)

unscreens	Oxybenzone	Sulisobenzone	Padimate O	Octyl Methoxycinnamate	Avobenzone
$_{max}$	287 nm	288 nm	310 nm	310 nm	358 nm
anges used (mg liter^{-1})	1–20	2–20	2.5–12	3–15	2.5–12
(slope)	0.0609	0.0417	0.1059	0.0864	0.1135
(intercept)	+0.0126	+0.0101	-0.0013	+0.0018	+0.0145
etermination coefficient, r^2	0.991	0.999	0.998	0.999	0.999
tandard deviation, s_b	0.0026	0.0005	0.0248	0.0009	0.0012
tandard deviation, s_a	0.0214	0.0046	0.0191	0.0081	0.0084
lope, 95% confidence limits (with appropiate t value)	[0.0543, 0.0675]	[0.0407, 0.0427]	[0.0977, 0.1142]	[0.0842, 0.0886]	[0.1105, 0.1164
ntercept, 95% confidence limits (with appropriate t value)	[-0.0425, 0.0677]	[-0.0002, 0.0204]	[-0.0628, 0.0597]	[-0.0174, 0.0211]	[-0.0055, 0.0346

RESULTS AND DISCUSSION

Five UV filters have been studied in vitro, in order to evaluate their photostability in different solvents. In the present case, 4 solvents and 2 associated emulsions (O/W and W/O) have been chosen. The kinetic degradation of each irradiated UV filter can be compared to the reference sample (sample at time 0, without irradiation). Due to the variability of UV filter concentrations used in the 4 solvents and 2 emulsions, it is worth comparing the photostability of each sunscreen in each solvent to its reference sample. Data were converted to percentage of recovery and 100% corresponds to the reference sample. All data are reported in Table 5.

Oxybenzone

The kinetic degradation (Fig. 2) provides an extreme photostability of oxybenzone in isopropyl myristate and propylene glycol. In paraffin oil, a moderate degradation of approximately 15% is observed in 4 hr. On the contrary, this filter seems to be stable for 2 hr in coconut oil, and then an important loss reaches 54% after 4 hr of irradation. Globally, both the formulations show a photodegradation (20%), and this lack of stability can be explained by the important quantities of coconut oil and paraffin oil in the emulsions, apolar solvents, where the sunscreen is not stable.

Sulisobenzone

This UV filter has a high stability in propylene glycol solvent (Fig. 3), one that is hydrophilic and soluble. The loss during the solar irradiation is extremely low from 0 to 4 hr with a little decrease after 2 hr (5%).

Sulisobenzone in O/W emulsion showed a significant degradation (31%). On the contrary, when sulisobenzone is formulated in the internal phase (W/O emulsion), this sunscreen is more stable. This result suggests that a water-soluble product will be protected in W/O formulation.

Padimate O

Padimate O showed a significant degradation in isopropyl myristate (24%) and a less significant degradation in coconut oil (13%) at 4 hr (Fig. 4). There is practically no degradation in paraffin oil. Padimate O has excellent photostability in O/W emulsion, and exhibits a small degree of degradation in W/O emulsion.

Octyl Methoxycinnamate

According to its solubility in all 4 solvents, there is a great degradation within two of them: propylene glycol and isopropyl myristate, with a loss of 33% and 30%, respectively, at 4 hr of irradiation (Fig. 5). Despite this decrease, it shows an interesting photostability in paraffin liquid and coconut oil, two lipophilic and apolar oils. In evaluation of both emulsions, a shift is observed. O/W emulsion is clearly stable; on the contrary, W/O emulsion loses nearly 40% at 4 hr.

Table 5

Kinetic Degradation: Percent of Degration, 100% Correspond to the Reference Sample "Time o".

	% Degradation of Each Sunscreen at 4 Time Points																								
	Oxybenzone					Sulisobenzon					e Padimate O					Octyl Methoxycinnamate					Avobenzone				
	0 min	30 min	60 min	120 min	240 min	0 min	30 min	60 min	120 min	240 min	0 min	30 min	60 min	120 min	240 min	0 min	30 min	60 min	120 min	240 min	0 min	30 min	60 min	120 min	240 min
Paraffin liquid	100	79.5	91.8	76.1	86.1	—	—	—	—	—	100	98	94	93.7	92.4	100	99.2	86.9	86.1	82.1	—	—	—	—	—
(standard error)	1.9	1.2	3.1	4.0	0.5						2.3	3.9	5.4	2.4	1.8	1.9	2.4	2.7	4.3	3.1					
Propylene glycol	100	102	104	102	107	100	99	99.9	93.7	91.6	—	—	—	—	—	100	88.4	86.7	85.2	67.1	—	—	—	—	—
(standard error)	9.9	1.1	11.6	2.5	5.5	9.7	3.3	5.7	5.2	3.8						2.0	1.2	4.0	6.2	1.7					
Coconut oil	100	105	109	105	49	—	—	—	—	—	100	99.7	98	90.7	86.7	100	85.3	83.9	79.5	79.4	—	—	—	—	—
(standard error)	4.8	5.1	8.0	2.8	3.5						0.7	1.7	1.4	1.7	2.6	0.2	3.1	0.4	3.1	1.3					
Isopropyl myristate	100	101	103	90.7	103	—	—	—	—	—	100	95.7	95.7	88	76.5	100	87.4	83.7	77	69.8	100	96.7	93.8	81.8	86.4
(standard error)	5.4	1.5	5.6	1.6	1.3						1.1	3.0	1.3	0.4	0.6	3.8	3.4	3.2	4.5	0.7	1.5	0.5	0.2	3.8	3.2
O/W emulsion	100	90.4	75.9	79.1	77.6	100	81.4	86.9	76.7	68.6	100	95.6	101	100	102	100	102	97.2	106	94.1	—	—	—	—	—
(standard error)	1.2	7.6	3.6	7.6	6.5	4.3	4.1	2.4	9.2	9.5	2.5	8.3	13.9	11.6	14.2	2.7	3.7	5.6	4.4	6.7					
W/O emulsion	100	96.4	86.1	87.7	85	100	94.3	94.4	93.6	80.6	100	99	99.4	93	86.3	100	90.3	93.5	90.3	61.1	—	—	—	—	—
(standard error)	10.1	2.4	9.1	4.9	1.5	1.3	1.6	0.9	1.8	2.3	1.6	4.3	5.8	5.1	9.1	5.9	6.2	3.1	4.1	1.1					

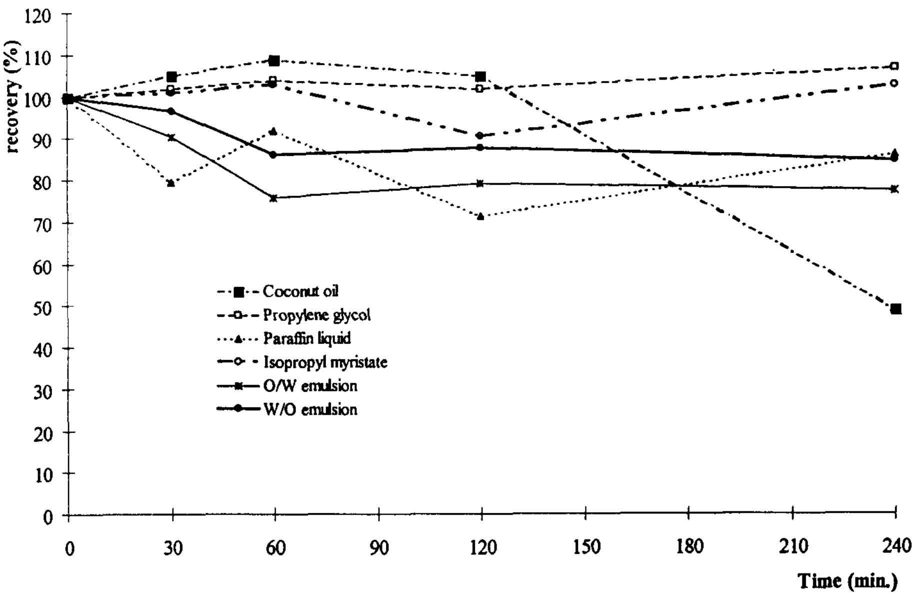


Figure 2. Oxybenzone kinetic degradation in solvents and emulsions.

Avobenzone

The difficult solubility in many solvents in our conditions leads to study of this filter in isopropyl myristate only, in which it shows a relative photostability with a loss of 12% after 4 hr (Fig. 6). No emulsion can be realized with this filter.

Photodegradation varies greatly from sunscreen to sunscreen, and generally, it is dramatically affected by the solvent vehicle according to previous results given

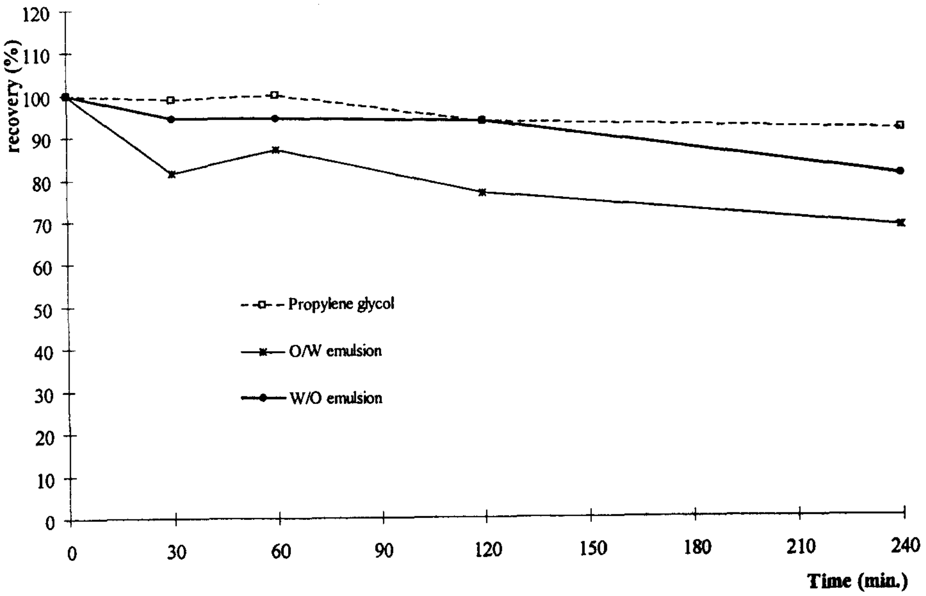


Figure 3. Sulisobenzone kinetic degradation in solvent and emulsions.

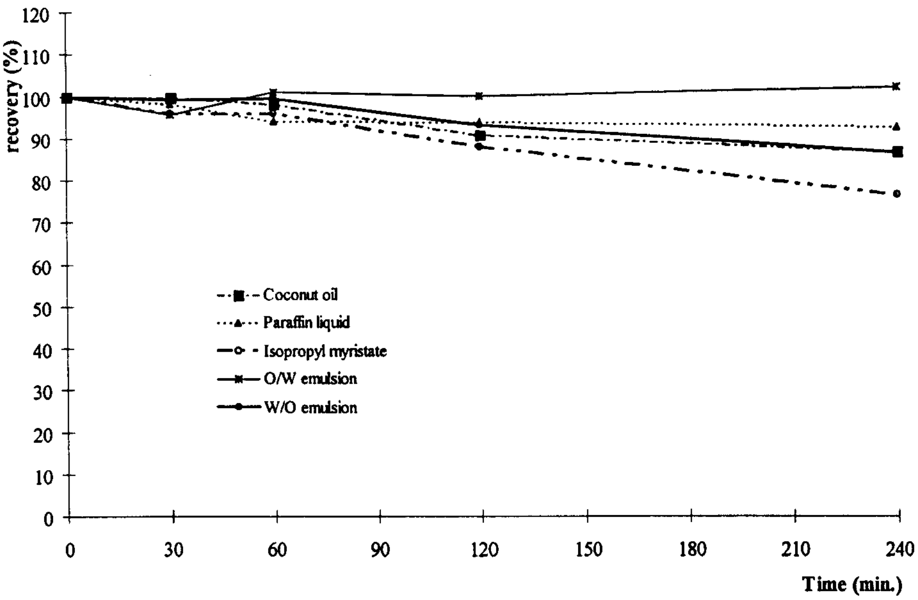


Figure 4. Padimate O kinetic degradation in solvents and emulsions.

by Shaath (15). We endeavored to determine the influence of different emulsion formulations on sunscreen photostability. In a major finding, we exhibited a shift between O/W and W/O formulations. This difference is extremely interesting. Good performances of O/W emulsions for nonpolar soluble UV filters shows that sunscreens are protected by emulsification only when the oily phase is dispersed in water phase. On the other hand, water-soluble sunscreen would be extremely suited to W/O emulsions. Photodegradation is dramatically increased when sunscreens are solubilized in the external phase of the emulsion.

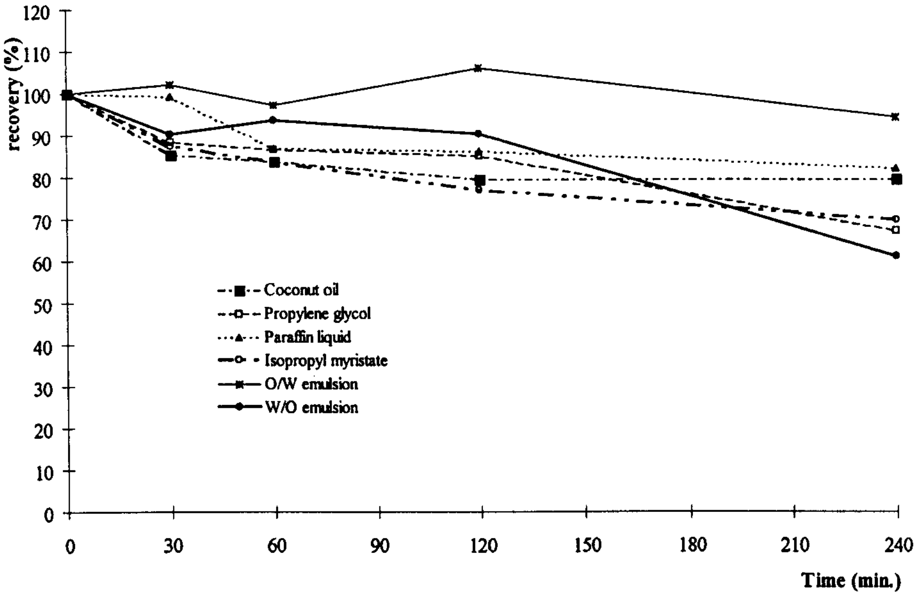


Figure 5. Octyl methoxycinnamate kinetic degradation in solvents and emulsions.

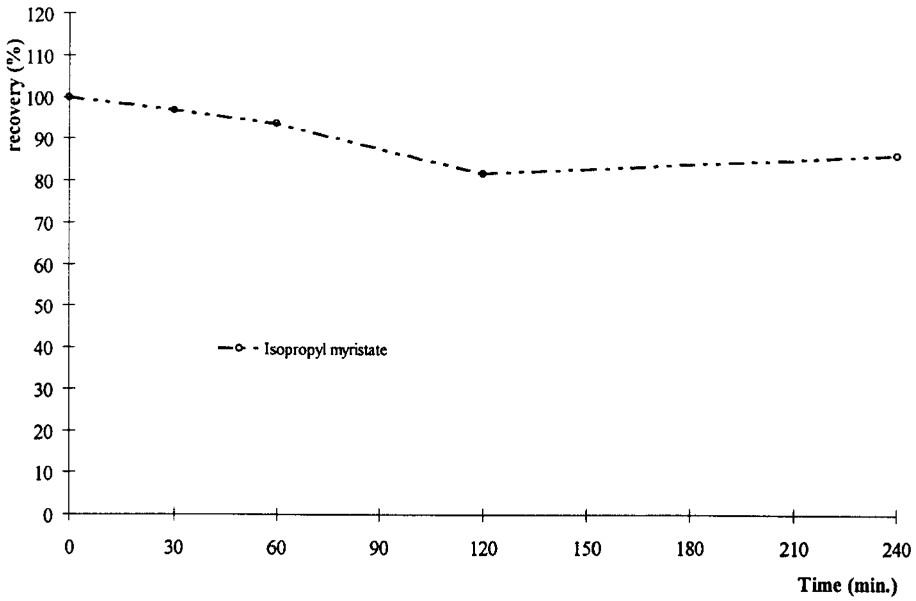


Figure 6. Avobenzone kinetic degradation in isopropyl myristate.

CONCLUSION

This study of photostability of sunscreens in 4 solvents provides practical information that might be useful in the formulation of sunscreen preparations, like emulsions. Therefore, the UV filters that are slightly soluble in different solvents such as avobenzone, reduce the choice in the formulation of emulsions, and their use is quite limited. The sunscreen should have excellent photostability and be photochemically inert and compatible with cosmetic vehicles. It seems that the formulation interacts positively on the photostability of UV filters. The results of this study show various degrees of degradation for each solvent and sunscreen. Meanwhile, emulsification of sunscreen in the internal phase protects it from photodegradation.

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