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## UV Spectrometric Study on a Synergetic System of Polymer Additives

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**Abstract:** An UV spectrometric method for the determination of the light stabilizer and the antioxidant from polymeric blends was developed. The investigated antioxidant and light stabilizer were: 2,2'-Methylene bis (6-tertbutyl-4-methylphenole), noted MBP and Tinuvin P (2-(2'-Hydroxy-5'-methylphenyl)-benzothiazole), noted TP. The described procedure works without any separation step of MBP and TP from each other and from the other polymer additives (namely stearic acid and paraffin). The second derivative signal measured at 281 nm was used for the elimination of the interferences of the other additives in the MBP estimation, while for determination of TP, the first derivative was measured at 326 nm. Beer's law has been valid in the concentration range of 1.5-30 ppm MBP and 1.0-30 ppm TP. The proposed method has been applied to the determination of MBP and TP in synthetic binary and tertiary mixtures and in polymeric blends with certified formula.

**Key words:** Polymer additives, antioxidant, light stabilizer, derivative spectrometry

### INTRODUCTION

Packaging has become an indispensable element in the food manufacturing process. Modern plastic packing for food must be seen as something more than simply an alternative for the paper bag or the glass bottle. For this reason, the development of high technology polymer systems occupies a place of prominence in the packing industry for food. In order to protect such as commercial polymers against aging and degradation, they are usually compounded with UV-stabilizers, antioxidants and lubricants. The principal material used for food packaging is Linear Low Density Polyethylene (LLDPE), which is produced by copolymerisation of ethylene with other olefins chosen from propylene, 1-butene, 4-methyl-1-pentene, 1-hexene or 1-octene, or a mixture of these alkenes. LLDPE films also contain one or more antioxidants, which prevent the oxidative degradation of the polymer. In such polyolefin films the most frequently encountered antioxidants are the phenol-based materials (Lawson *et al.*, 1996). They are compounded into the polymer typically at around the 0.1-0.5% (weight for weight) level. Other additives include light stabilizers. Recent studies report that several UV stabilizers show a synergism with phenolic antioxidants. In such cases, the additions of these synergetic systems can lead to an

improvement of the polymer stability of a factor of 2-3 (Gijsman, 2002). Once incorporated into the polyolefins, an analytical estimation of the polymer additives is of a real interest. This, for the quality controls of the polymeric blend and taking into account the possible toxicity of these additives.

Various techniques for determination of polymeric light stabilizers and antioxidants have been introduced in recent years. The analysis of these additives may be carried out by non-destructive spectrometric (in-polymer) testing of solid or melt (Girois *et al.*, 1999; Konstantinova *et al.*, 1994), or by destructive testing using thermal methods (thermal analysis, pyrolysis, mainly through the examination of volatiles released, thermal desorption or highfinated techniques (Py-GC, Py-MS, Py-GC-MS) (Bart, 2001; Herrera *et al.*, 2003; Coulier *et al.*, 2005). Other papers report the analysis of the polymer additives by the examination of extracts, using chromatographic methods (HPLC) (Marcato and Vianello, 2000; Matz, 1991); coupled Thin-Layer Chromatography (TLC) and FT-IR microscopy (He *et al.*, 2002); supercritical fluid extraction with on-line coupling of reversed-phase liquid chromatography (Ashraf-Khorassani *et al.*, 2003); coupled size-exclusion-normal phase HPLC (Nerin *et al.*, 1995); capillary temperature-programmed liquid chromatography (Trones *et al.*, 2000).

Although, high selectivity and sensitivity characterize chromatographic or coupled techniques, they still do not satisfy all requirements for routine analysis, mainly because of their complicated process design, time consumption or the need for expensive instruments. But, many analytical laboratories have not such expansive instruments. Almost all these laboratories have at least a spectrometer. So, an alternative for the quality control of a kind of polymer mixture (having a known composition) could be represented by a spectrometric method. The main parameters verified in the quality control of polymer mixtures, with certified formula, is the content of the antioxidant and light stabilizer (taking into account their toxicity). This is the reason for which, in the past years, we have proposed a series of spectrometric methods for determination of some polymer additives, in specific real samples (Moldovan and Alexandrescu, 2002a, b; Moldovan *et al.*, 2005), taking into account that the polymer additives have UV spectrometric properties. In this study, we have proposed the UV derivative spectrometric method for estimation of the antioxidant and the light stabilizer, without any separation step from each other and from the plasticizers. As it is well known, by applying this technique, interferences in the direct ultraviolet molecular absorption spectrometry could be minimized or even avoided. The method is not new but it was applied by the authors of this study in the research of polymer additives (Ojeda and Sanchez Rojas, 2004).

## MATERIALS AND METHODS

All the chemicals used were of analytical-reagent grade (Merck) and all the solutions were prepared in chloroform. One type of polymer was used, namely Linear Low Density Polyethylene (LLDPE). The specimen of polymer was manufactured specifically for this study. The polymer extraction was made in acetone. As light stabilizer, Tinuvin P (2-(2'-Hydroxy-5'-methylphenyl)-benzothiazole, noted TP) was selected. The antioxidant used was 2,2'-Methylene bis (6-tertbutyl-4-methylphenole), noted MBP. As, further processing aids, stearic acid (SA) and paraffin (P) were used. Stock solutions of polymer additives (100 ppm) were prepared in chloroform. Working solutions were obtained by appropriate dilutions of the stock solutions with chloroform.

All absorption spectra and derivatives were recorded with a Jasco-V 530 UV-VIS double beam spectrometer, equipped with a pair of 1 cm path length quartz cells and interfaced to a compatible computer running spectrometric software. This equipment allows a direct derivatization up to the third-order. The suitable wavelength at which

derivative spectrum crosses the zero-line was linearly approximated from two neighboring measurements. Suitable settings were: Slit width, 1 cm; scan speed, 200 nm min<sup>-1</sup>.

Preparation of polymeric blends and the extraction procedure were made at Research Development National Institute for Textile and Leather-Division Leather and Footwear Research Institute and the proposed spectrometric method was conducted at Department of Analytical Chemistry, University of Bucharest, Faculty of Chemistry Bucharest, Romania in the year 2006.

**Procedure for spectra measurements:** Suitable volumes of stock solutions (100 ppm) of polymer additives were placed into the 10 mL calibrated flasks and brought to volume with chloroform. Also, mixtures of stock solutions containing suitable amounts of the investigated polymer additives were placed into the 10 mL standard flasks and diluted to the mark with chloroform. The absorption spectra of the samples were recorded in the range 250-350 nm, against chloroform. For the determination of the antioxidant (MBP), the value of the second derivative spectra was measured at the selected zero-crossing wavelength of the second derivative spectra of the other polymer additives presented in mixtures ( $\lambda = 281$  nm) and compared with the calibration graph. In the same way, the light stabilizer (TP) was determined on the basis of its first derivative signal, measured at 326 nm and compared with its proper calibration graph. TP was also estimated on the basis of the absorbance measured at 341 nm.

**Preparation of polymeric blends:** The polymeric blends were manufactured with the additives in a certified formula. Thus, the ingredients were added to obtain a formulation which could be manufactured under normal industrial conditions, in the following proportions: polymer (Linear Low Density Polyethylene (LLDPE)), 500; zinc oxide, 20; calcium carbonate, 50; TP, 3; MBP, 3; stearic acid, 40; paraffin, 40. Preparation of the polymeric blends takes place by compounding them in an extruder granulator, under specific technological conditions (temperature of approximately 80°C; granulation rate, 120 rotations min<sup>-1</sup>; time, 20 min).

**Extraction:** Extraction was performed on a weighed amount of the polymeric specimen (3 g, cut into small pieces), in a Soxhlet extractor for 24 h, with a defined volume of acetone, at the boiling temperature of the solvent. In order to minimize the decomposition and loss of the polymer additives during extraction, this was made under nitrogen. After evaporation to dryness in a vacuum, the obtained extract was dissolved in chloroform, filtered

and then diluted, in order to be recovered with chloroform in a 100 mL calibrated flask. A 2.5 mL portion of this solution was diluted to 50 mL with chloroform and the spectrum recorded.

**Conformance to Beer's law:** Into each of a series of 10 mL calibrated flasks, known volume of polymer additive solution (MBP or TP) was transferred, diluted to the mark with chloroform and mixed. The absorption spectra of these solutions were recorded. The values of the absorbance at 341 nm were used for preparation of calibration graph for TP estimation. Then, the first derivative was applied and the analytical signal attributed to TP was measured at  $\lambda = 326$  nm. For estimation of MBP, the second derivative was applied and measured at  $\lambda = 281$  nm.

## RESULTS AND DISCUSSION

**Absorption spectra of the polymer additives:** As it is known, many polymer additives absorb UV radiations and therefore they have characteristic UV spectra. Thus, the analysis of the antioxidant (MBP) and of the light stabilizer (TP) could be performed by a spectrometric method, after preliminary separation of all additives from the polymer matrix (this separation is made by solid/liquid extraction in a Soxhlet extractor). But, as it is shown in Fig. 1, UV-conventional spectra of MBP and TP overlap considerably between 260 and 300 nm, while the two processing additives (stearic acid, noted SA and paraffin, noted P) have small absorbances on the whole studied wavelength range. Also, at  $\lambda = 341$  nm, corresponding to the maximum absorbance of TP, the other polymer additives have small values of absorbance.

**Derivative spectral characteristics of the investigated additives:** In order to prevent the effect of spectral interferences in MBP estimation, the UV derivative spectrometry was proposed. The most common technique used for quantitative analysis is the Zero-Crossing Method (ZCM). This method involves a measurement of the amplitude of the total derivative spectrum at an abscissa value ( $\lambda$ ) corresponding to the Zero-Crossing Point (ZCP) of the interfering components. So, at this wavelength, the derivative signal attributed to the interferences passed through zero. To obtain the wavelength at which TP crosses the zero-line and MBP presents analytical signal, we have applied the derivatives of different orders to the recorded UV-conventional spectra of the investigated additives. Thus, as is shown in Fig. 2, the second derivative was chosen to be proper for our analytical purpose. So, for MBP estimation, the

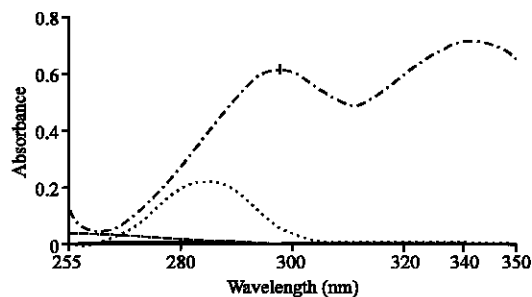


Fig. 1: Conventional UV spectra of the polymer additives. TP (dotted-dashed line); MBP (dotted line); SA (dashed line); P (continuous line)  $c_{TP} = c_{MBP} = 10$  ppm;  $c_P = c_{SA} = 250$  ppm

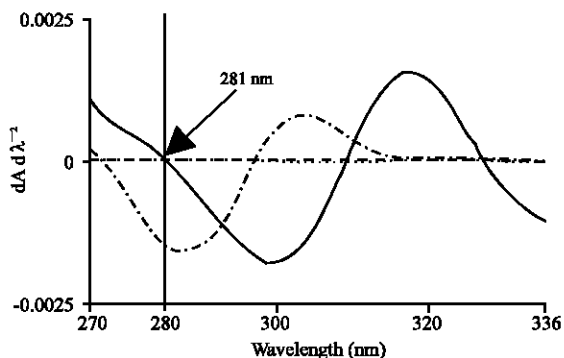


Fig. 2: Second derivative spectra of the polymer additives. TP (continuous line); MBP (dotted-dashed line); P (dotted line); SA (dashed line);  $c_{TP} = c_{MBP} = 10$  ppm;  $c_P = c_{SA} = 250$  ppm

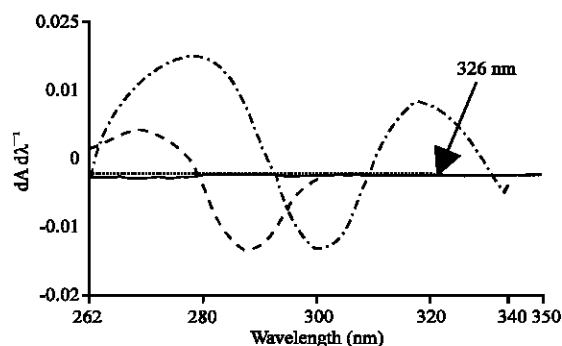


Fig. 3: First derivative spectra of the polymer additives. TP (dotted-dashed line); MBP (dashed line); P (dotted line); SA (continuous line);  $c_{TP} = c_{MBP} = 10$  ppm;  $c_P = c_{SA} = 250$  ppm

second derivative signal was measured at  $\lambda = 281$  nm. At this wavelength, the second derivative spectrum of TP crosses the zero-line, while the value of the derivative

signal of MBP allows its quantification. Also, as we observe in the Fig. 1, the simple measurement of absorbance at  $\lambda = 341$  nm could be used for estimation of TP in presence of the other polymer additives. For a better accuracy, TP could be determined by measuring the first derivative of absorbance at  $\lambda = 326$  nm (Fig. 3).

**Calibration plots: Analytical performance characteristics:**

Ten standard solutions having concentrations between 0 and 35 ppm were prepared, for each individual analyte (MBP and TP, respectively). Both sets of solutions were analyzed by the proposed methods and the range of linear dependence of the spectrometric response on concentration was found for each analyte. The intercepts for all calibration graphs were almost passing through the origin. The main spectral characteristics used for estimation of MBP and TP are presented in Table 1. The precision for five replicate analyses of 10 ppm of polymer additive was as follows: for TP,  $\pm 2.28\%$  (by measuring the absorbance) and  $\pm 3.28\%$  (by applying the first derivative); for MBP,  $\pm 3.25\%$ . The Limit Of Quantification (LOQ) for the two analytes were determined as the lowest concentration showing a coefficient of variance (CV) values less than 5%.

**Determination of TP and MBP in synthetic mixtures:**

In a first stage, binary mixtures TP: MBP = 1:1 were analyzed by the proposed spectrometric methods. The results in Table 2 show that a ratio of 1:1 allows the determination of both polymer additives, with good results, in the

following concentration ranges: 1.5-30 ppm TP (by measuring the absorbance or by applying the first derivative) and 1.5-15 ppm MBP. The recoveries obtained were as follows: for TP, 98.66-105.26% (RSD (Relative Standard Deviation) = 0.01-4.25%) by measuring the absorbance and 99.60-101.80% (RSD 0.02-0.07%) by applying the first derivative, in the concentration range 1.5-30 ppm and for MBP, 96.80-105.87% (RSD = 0-2.84%) in the concentration range 1.5-15 ppm.

In a second stage, different TP -to- MBP ratios were tested to check for the presence of mutual effects. Thus, it was maintained a constant concentration of one of the two additives in the presence of the other, over a range of concentrations between 2.5 and 10 ppm (to obtain a 1:2 to 1:4 ratio between the 2 investigated analytes). Then, the conventional spectra of binary mixtures, obtained against chloroform, were recorded and transformed in the first and second derivative, respectively. The concentrations of TP and MBP were estimated as presented in the general procedure. As it can be seen in Table 3, TP can be determined in the presence of a 4 fold excess of MBP both by measuring the absorbance and the first derivative. By applying the first derivative, the experimental results for TP are more close to those calculated. For this reason, the determination of TP in real samples was performed only on the basis of its first derivative signal. In the case of MBP, it can be determined with good precision and accuracy, in the concentration range 2.5-10 ppm and in the presence of TP, even the ratio TP:MBP = 4:1. At higher concentration, the excess of TP leads to a decrease of the accuracy in the determination of MBP.

Table 1: Spectral characteristics of TP and MBP

Characteristics of calibration graphs						
Analyte	Function	$\lambda^*$ (nm)	Linear regression equation	LOQ (ppm)	Correlation coefficient (R <sup>2</sup> )	Conformance to Beer's law (ppm)
TP	A = f(c)	341	y = 0.0726x + 0.0006	0.1	0.998	0.05-30
	dA/d $\lambda$ = f(c)	326	y = 0.0012x + 0.0004	1.0	0.9991	1-30
MBP	d <sup>2</sup> A/d $\lambda^2$ = f(c)	286	y = -0.0001x - 0.00005	1.5	0.9970	1.5-30

\*Wavelength at which the measurement of the analytical signal was made

Table 2: Results of TP and MBP determination in binary mixtures (ratio of 1:1)

Analyte in sample (ppm)	TP				MBP	
	By measuring A ( $\lambda = 341$ nm)		By measuring dA/d $\lambda$ ( $\lambda = 326$ nm)		Found (ppm)	Recovery $\pm$ RSD (%) (n = 3)
	Found (ppm)	Recovery $\pm$ RSD (%) (n = 3)	Found (ppm)	Recovery $\pm$ RSD (%) (n = 3)		
1.5	1.48	98.66 $\pm$ 0.18	1.52	101.33 $\pm$ 0.02	1.50	100.00 $\pm$ 0.00
2.5	2.49	99.60 $\pm$ 0.08	2.49	99.60 $\pm$ 0.07	2.42	96.80 $\pm$ 2.84
5	4.99	99.80 $\pm$ 0.13	5.09	101.80 $\pm$ 0.04	5.19	103.80 $\pm$ 0.13
10	9.99	99.90 $\pm$ 0.01	10.07	100.70 $\pm$ 0.02	10.43	104.30 $\pm$ 0.72
15	15.10	100.66 $\pm$ 0.24	15.18	101.20 $\pm$ 0.07	15.88	105.87 $\pm$ 0.24
20	19.99	99.95 $\pm$ 1.76	20.00	100.00 $\pm$ 0.15	21.61	108.05 $\pm$ 1.98
25	25.51	102.04 $\pm$ 3.26	25.11	100.44 $\pm$ 0.13	27.33	109.32 $\pm$ 3.26
30	31.58	105.26 $\pm$ 7.41	30.05	100.16 $\pm$ 0.08	32.43	108.10 $\pm$ 7.41

Table 3: Result of TP and MBP determination in binary mixtures (in different ratios)

Analyte in sample (ppm)	Conc. of analyte (ppm)	TP				MBP	
		By measuring A ( $\lambda = 341$ nm)		By measuring dA/d $\lambda$ ( $\lambda = 326$ nm)		Found (ppm)	Recovery $\pm$ RSD (%) (n = 3)
		Found (ppm)	Recovery $\pm$ RSD (%) (n = 3)	Found (ppm)	Recovery $\pm$ RSD (%) (n = 3)		
1:2	2.5	2.48	99.20 $\pm$ 3.80	2.50	100.00 $\pm$ 0.00	2.50	100.00 $\pm$ 3.25
1:3		2.58	103.20 $\pm$ 2.15	2.50	100.00 $\pm$ 0.00	2.52	102.00 $\pm$ 2.64
1:4		2.62	104.80 $\pm$ 3.72	2.50	100.00 $\pm$ 0.00	2.55	104.80 $\pm$ 3.14
1:2	3	4.96	99.20 $\pm$ 0.74	5.00	100.00 $\pm$ 0.00	5.11	102.20 $\pm$ 3.32
1:3		4.96	99.20 $\pm$ 2.15	5.00	100.00 $\pm$ 0.00	5.12	102.40 $\pm$ 4.15
1:4		5.25	105.00 $\pm$ 2.72	5.00	100.00 $\pm$ 0.00	5.14	103.00 $\pm$ 3.48
1:2	10	9.93	99.20 $\pm$ 1.85	9.97	99.70 $\pm$ 1.13	10.40	104.00 $\pm$ 2.84
1:3		10.35	103.20 $\pm$ 2.15	10.05	100.00 $\pm$ 2.55	10.35	103.50 $\pm$ 2.63
1:4		10.55	105.00 $\pm$ 2.72	10.11	100.40 $\pm$ 2.73	10.34	103.40 $\pm$ 3.17
2:1	2.5	2.50	100.00 $\pm$ 0.12	2.49	99.60 $\pm$ 0.15	2.63	105.20 $\pm$ 2.85
3:1		2.52	100.80 $\pm$ 0.18	2.50	100.00 $\pm$ 0.00	2.72	108.80 $\pm$ 3.54
4:1		2.53	101.20 $\pm$ 0.58	2.51	110.40 $\pm$ 0.00	2.78	111.20 $\pm$ 3.58
2:1	5	5.05	101.00 $\pm$ 0.74	5.05	101.00 $\pm$ 0.24	5.20	104.0 $\pm$ 3.24
3:1		5.07	100.40 $\pm$ 2.15	5.10	102.00 $\pm$ 1.51	5.35	107.0 $\pm$ 3.24
4:1		5.07	101.40 $\pm$ 2.72	5.12	102.40 $\pm$ 0.24	5.65	113.0 $\pm$ 3.24
2:1	10	9.97	99.70 $\pm$ 0.74	9.98	99.80 $\pm$ 1.76	10.75	107.50 $\pm$ 1.98
3:1		9.96	99.60 $\pm$ 2.15	10.00	100.00 $\pm$ 2.45	10.85	108.50 $\pm$ 2.76
4:1		10.07	10.02 $\pm$ 2.75	10.02	100.20 $\pm$ 2.56	11.20	112.00 $\pm$ 3.15

Table 4: Results of TP and MBP determination in tertiary mixtures

Conc. of analyte (ppm)	TP				MBP	
	By measuring A ( $\lambda = 341$ nm)		By measuring dA/d $\lambda$ ( $\lambda = 326$ nm)		Found (ppm)	Recovery $\pm$ RSD (%) (n = 3)
	Found (ppm)	Recovery $\pm$ RSD (%) (n = 3)	Found (ppm)	Recovery $\pm$ RSD (%) (n = 3)		
5	5.55	111.00 $\pm$ 0.03	5.02	100.40 $\pm$ 0.24	5.00	100.00 $\pm$ 0.00
10	10.75	107.50 $\pm$ 0.24	10.02	100.20 $\pm$ 0.16	10.62	106.20 $\pm$ 0.00

Table 5: Results of MBP and TP determination in real sample

In sample	Conc. of analyte (g per 100 g of sample)			
	TP <sup>a</sup>		MBP <sup>b</sup>	
	Found	Recovery $\pm$ RSD (%) (n = 3)	Found	Recovery $\pm$ RSD (%) (n = 3)
0.46	0.44	95.65 $\pm$ 3.26	0.39	84.78 $\pm$ 5.25

<sup>a</sup>The first order derivative spectrometry was applied at 326 nm, <sup>b</sup>The second order derivative spectrometry was applied at 281 nm

On the basis of the obtained results and taking into account that in real polymeric blends the mentioned additives are introduced together with stearic acid and paraffin, a series of synthetic tertiary mixtures were prepared and the proposed method applied for MBP and TP estimation. In the prepared mixtures, the ratios were as in real samples (MBP-TP-SA-P = 1:1:13:13). The results obtained are summarized in Table 4. The proposed spectrometric method applied to tertiary mixtures of polymer additives allows the determination of MBP and TP, one in presence of the other constituents, in the investigated concentration range. The recoveries obtained were as follows: For TP, in the range 107.5-110.93 % (RSD = 0.03-0.24%) by measuring the absorbance and 100.2-100.4% (RSD = 0.16-0.24%) by applying the first derivative and for MBP, 100-106.2%.

The results in Table 4 suggest that the proposed spectrometric method can be applied for practical use. In order to evaluate its efficiency, the proposed spectrometric method was applied to real samples of polymeric blends (having certified formula), according to the general procedure. As we observe in the mentioned procedure, a minimum 20 fold dilution of the sample is required, taking into account the concentration range for the method proposed here.

The recovery of the analytes was found to be: 95.18 $\pm$ 3.26% for TP and 84.68 $\pm$ 5.25% for MBP (three determinations). A lower recovery of MBP from real samples was obtained. It could be assumed that this behavior arises from the fact that antioxidants are labile unstable compounds forming complex decomposition products (Wheeler, 1968). So, any loss of material is liable

to be significant since the quantity of antioxidant present is initially so low. This results in a decrease of free MBP in polymeric mixtures and therefore in extract. So, for quantitative estimation of MBP in unknown samples (containing the mentioned polymer additives), a correction factor can be applied on the results obtained by the proposed method. On the basis of the results listed in Table 5, this correction factor was found to be 1.18.

## CONCLUSIONS

The proposed spectrometric method permits the estimation of the antioxidant MBP and the light stabilizer TP in tertiary mixtures without separation from the other polymer additives. Derivative spectrometry, as fast, simple and easy accessible technique, seems to be an efficient method that may be used in routine analysis of the antioxidant and the light stabilizer in multicomponent polymeric mixtures with certified and specific formula. So, the described technique can be applied in the quality control of these polymeric materials.

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