



# Photochemical weathering study of Brazilian petroleum by EPR spectroscopy

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## Abstract

The EPR spectrum of the petroleum of the Campos Basin, Rio de Janeiro, Brazil shows signals characteristic of free radical, vanadyl ( $\text{VO}^{2+}$ ) and iron III ion ( $\text{Fe}^{3+}$ ). The value of  $g=2.0045 \pm 0.0001$  corresponds to free radical species with a peak-to-peak line width  $\Delta H=4.64 \pm 0.03$  G. The  $g$  spectroscopic factor suggests the presence of free radicals in aromatic systems containing carbon, nitrogen and oxygen.  $\Delta g_o$  (chemical shift)  $=21.6 \pm 0.1$  determined for the  $\text{VO}^{2+}$  species characterizes porphyrin and non-porphyrin (with sulfur) complexes in asphaltenes of the crude oil. The species observed with  $g=2.16 \pm 0.01$  corresponds to  $\text{Fe}^{3+}$  in  $\text{Fe}_2\text{O}_3$ , and therefore is not part of the molecular structure of the oil under study. The photochemical weathering of Brazilian oil as a film over seawater was monitored by EPR. After 100 h of solar irradiation the line width of the radical decreased by 10.6%, indicating rearrangement among radicals. The  $\Delta g_o$  value for  $\text{VO}^{2+}$  in the irradiated oil decreased to  $19.5 \pm 0.1$ , characterizing degradation of porphyrin systems. Solar irradiation promotes the partial destruction of the asphaltenic fraction of the oil.

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## 1. Introduction

The environment has been a victim of human incautiousness all over the planet. Rivers, seas, soils, fauna and flora have been suffering with these happenings for the last decades, mainly due to accidents involving oil and its by-products. Over the last few

years, the most advanced industrialized nations have been facing problems related to the destination of dangerous residues (Rife et al., 1989). Among typical residues are aviation fuel, heavy metals, vehicle fuels, solvents, degrading agents and chemical by-products.

Spills of petroleum or its by-products are spectacular events in this scenario of pollution. The spilled oil suffers the action of the environment, with the occurrence of physical, chemical and biological effects (Nicodem et al., 1997). The oil spreads on the surface of rivers or seas forming a spot of variable thickness (from millimeters to micrometers) that dislocates

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according to the speed and direction of the winds, marine currents, etc. In its passage the spot suffers a series of weathering processes, which are influenced by other factors such as the condition and climate of the rivers or seas, the presence of bacteria and particulate material suspended in the water, and mainly the physicochemical properties of the oil.

The contamination of world water by oil and its by-products has been estimated at  $3.2 \times 10^6$  tons/year (Clark, 1989), 92% is directly related to human activities, and one eighth of this share is due to accidents with ship-tanks. The short- and long-term effects of this input have been the subject of serious concern and much research (National Academy of Sciences, 1985). In July 2000, an environmental accident occurred in the state of Paraná, Brazil, where 4 million liters of crude oil was spilled from the Getúlio Vargas refinery (REPAR/PETROBRAS) into the Barigüi and Iguacu rivers. Although in most cases the recovery of the environment after a large-scale oil spill is slow, the speed of recovery is different in each case, i.e. in sediments, rivers, beaches or open sea.

Since laboratory monitoring has shown photochemical degradation of crude oil, an efficient process for oil oxidation and removal must also occur in the environment (Guedes, 1998). Several scientific investigations have been carried out in an attempt to reduce the actual damages caused by-products that attack nature. In countries where the incidence of solar light is significant, the process of photochemical weathering is an important mechanism for the removal of foreign substances from the environment (Nicodem et al., 1998).

Photochemical transformations have been demonstrated to occur in petroleum when it is exposed to the environment. In tropical climates, where solar intensity is high and biological processes are hindered by the lack of nutrients, photochemical processes are the most important contributors to oil degradation (Ehrhardt et al., 1992). Moreover, photochemical processes can be important for subsequent biological oil consumption.

The effects of photochemical oxidation of petroleum films over water were studied by Nicodem et al. (2001). We studied by EPR (Guedes et al., 2001) the changes in Arabian and Brazilian petroleum caused by irradiation with a mercury vapor lamp and He–Ne laser.

In the present study we basically investigated Brazilian oil (Campos Basin, Rio de Janeiro, Brazil) exposed to sunlight under natural tropical conditions using EPR in order to obtain information about the molecular structure of crude oil.

## 2. Experimental

The petroleum used for this study was from a Campos Basin offshore oil field in the state of Rio de Janeiro, and was supplied to us by the Brazilian oil company, PETROBRAS. In all experiments, 5 ml of petroleum was placed floating over 20 ml of seawater. The resulting oil film was 0.8-mm thick. Petri dishes with Pyrex lids were used. This Pyrex® transmits 75% at 295 nm and 85% at 300 nm, with little sunlight attenuation (Nicodem et al., 1998). Its use is common practice for samples with considerable absorption in the UVA and visible portions of the solar spectrum (El Anba-Lurot et al., 1995; Lartiges and Garrigues, 1995; Nicodem et al., 1998). Crude oil absorbs sunlight in the ultraviolet, visible and near infrared, as reported by Nicodem et al. (1997). Samples were irradiated by exposure to sunlight on the laboratory's building roof on cloudless days from 9:00 AM to 3:00 PM, and were stored in the dark in a freezer at  $-15\text{ }^{\circ}\text{C}$  between irradiations until the total number of hours had been accumulated. Although storage at room temperature gave the same results, this precaution was taken to insure that there was no biological degradation after extended storage during cloudy periods. For every irradiated sample we used a non-irradiated control, which was handled in the same way except that a black cover plate was used to eliminate irradiation. After irradiation, the two phases were separated by centrifugation and the oil samples were stored in the dark at  $-15\text{ }^{\circ}\text{C}$  while awaiting analysis.

EPR experiments were performed at X-band (9.5 GHz) microwave frequency and at a magnetic field modulation of 100 kHz in Bruker® (ESP 300E Series) equipment at room temperature. Diphenyl picryl hydrazyl (DPPH) ( $g=2.0036$ ) was used as  $g$  marker and the microwave frequency was accurately read with an HP 5352B frequency counter. Petroleum was introduced in 4-mm quartz EPR tubes. A “cavity baseline”, i.e. an EPR spectrum of the empty cavity,

was obtained and did not show any signal. The magnetic field of the EPR instrument was calibrated periodically against a standard sample.

### 3. Results and discussion

The EPR spectrum of petroleum (Fig. 1A) showed signals of paramagnetic species such as vanadyl (Fig. 1B) and free radicals (Fig. 1C). A similar spectrum was shown by Scotti and Montanari (1998) for a sample of asphaltenes.

Fig. 1A also shows a very wide line, usually not observed in petroleum by EPR. Fig. 2 shows this same spectrum (continuous line) in an amplified range of the magnetic field which is compared to the EPR spectrum obtained by Glinchuk et al. (1994) for the Pb/Mg<sub>1/3</sub>Nb<sub>2/3</sub> ceramic doped with Fe<sub>2</sub>O<sub>3</sub> (dashed line).

The spectrum of vanadyl can be interpreted in terms of the following spin Hamiltonian with axial symmetry (O'Reilly, 1959):

$$H = g_{\parallel} \beta H_z S_z + g_{\perp} \beta (H_x S_x + H_y S_y) + A_{\parallel} S_z + B(I_x S_x + I_y S_y), \quad (1)$$

where  $S = 1/2$  and  $I(V^{51}) = 7/2$ .

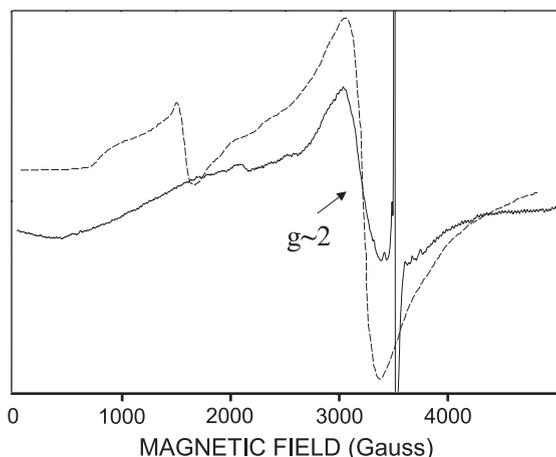


Fig. 2. The EPR spectrum of Brazilian petroleum obtained at room temperature with a broad scan range (0 to 5000 G) is shown by the continuous line and the spectrum of the Pb/Mg<sub>1/3</sub>Nb<sub>2/3</sub> ceramic doped with Fe<sup>3+</sup> is shown by the dashed line.

We determined the values of the EPR parameters for the species detected in the petroleum under study (Table 1). The uncertainty in the determination of the  $g$  values for VO<sup>2+</sup> and the free radical was  $\pm 0.0001$ .

The WINEPR SimFonia Version 1.25 software of Bruker® was used in the simulation option for the determination of  $g_{\parallel}$ ,  $g_{\perp}$ ,  $A_{\parallel}$  and  $A_{\perp}$  of the vanadyl species.

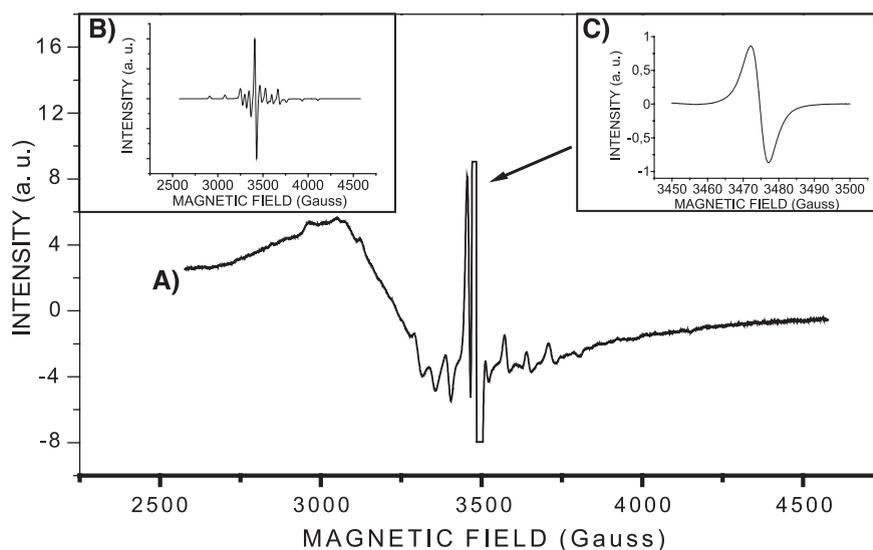


Fig. 1. (A) EPR spectrum of Brazilian petroleum at room temperature. Gain =  $1.0 \times 10^5$ . Number of scans = 7. (B) Simulated EPR spectrum of the VO<sup>2+</sup> species. (C) EPR spectrum of the free radical is pointed out using a smaller scan range. Gain =  $1.0 \times 10^3$ . Number of scans = 5.

Table 1  
EPR  $g$ -values for the paramagnetic species of Brazilian petroleum at room temperature

Specimen	$g$ -value	Sample	0 h	2 h	5 h	20 h	40 h	60 h	100 h
$\text{VO}^{2+}$	$g_{//}$	NI <sup>a</sup>	1.9675	1.9682	1.9685	1.9685	1.9685	1.9685	1.9685
	$g_{//}$	I <sup>b</sup>	1.9675	1.9690	1.9690	1.9690	1.9700	1.9700	1.9705
	$g_{\perp}$	NI	1.9873	1.9870	1.9870	1.9872	1.9875	1.9875	1.9875
	$g_{\perp}$	I	1.9873	1.9873	1.9877	1.9880	1.9885	1.9889	1.9889
	$g_o$	NI	1.9807	1.9807	1.9808	1.9810	1.9812	1.9812	1.9812
	$g_o$	I	1.9807	1.9812	1.9815	1.9817	1.9823	1.9826	1.9828
Free radical	$g$	NI	2.0045	2.0045	2.0045	2.0045	2.0045	2.0045	2.0045
	$g$	I	2.0045	2.0045	2.0045	2.0045	2.0045	2.0045	2.0045

<sup>a</sup> Non-irradiated.

<sup>b</sup> Irradiated.

When the molecule is rotating about with a correlation time much shorter than the reciprocal of the spread of the spectrum in frequency, Eq. (1) is reduced to an “isotropic” Hamiltonian, with  $g_o = (1/3)(g_{//} + 2g_{\perp})$  (O’Reilly, 1959).

There was no significant variation in the hyperfine interaction parameters  $\{A_{//} = (156.0 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}$  and  $A_{\perp} = (54.0 \pm 0.1) \times 10^{-4} \text{ cm}^{-1}\}$  in any of the samples (irradiated and non-irradiated).

No variations in  $g$  values were observed in non-irradiated samples for any of the paramagnetic species (Table 1). The line width ( $\Delta H$ ) or peak-to-peak separations of the EPR derivative peaks did not show variations for the free radical. The uncertainty in the determination of the  $\Delta H$  for the free radical was  $\pm 0.03 \text{ G}$ .

An increase in the  $g_o$  values for  $\text{VO}^{2+}$  was observed in irradiated samples (Table 1). There was no

variation in the  $g_o$  values for the free radical, whereas the line width ( $\Delta H$ ) showed a significant decrease (Fig. 3).

### 3.1. $\text{VO}^{2+}$ specimen

The EPR spectra of some petroleum samples show lines of hyperfine interaction that assist in the identification of the porphyrin or non-porphyrin vanadium complexes in crude oil (Saraceno et al., 1961; Espinosa et al., 2001).

$\Delta g_o$  (chemical shift), which expresses chemical changes, was calculated from the spectroscopic factors  $g_o$   $\{\Delta g_o = (2.0023 - g_o) \times 10^3\}$  (Dickson and Petrakis, 1974). The different values obtained experimentally for the  $\Delta g_o$  parameter represent structural differences in the distribution of the ligands around the  $\text{VO}^{2+}$  in complexes. The value obtained for vanadium in the

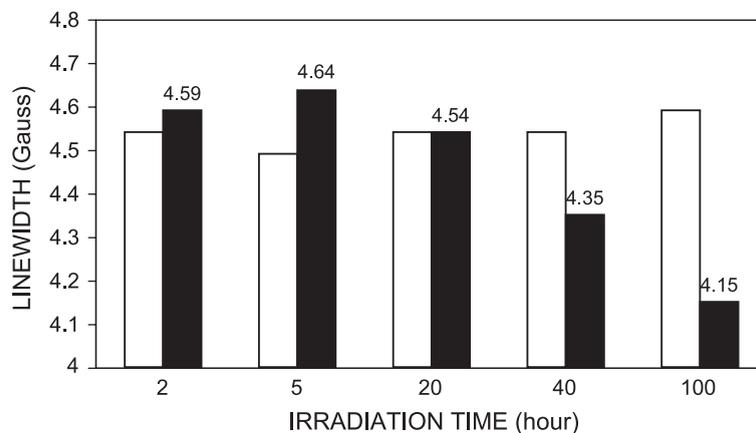


Fig. 3. Variation of the line width of the free radical versus sunlight irradiation time. Filled columns represent the irradiated samples and blank columns the non-irradiated samples.

benzene eluate,  $\Delta g_o = 22.3$ , is representative of vanadyl porphyrins (Boucher et al., 1969; Dickson et al., 1972).

The value experimentally obtained for the Brazilian oil was  $\Delta g_o = 21.6$ , indicating that this oil contains vanadyl in the porphyrin and non-porphyrin structures. Based on literature data (Dickson and Petrakis, 1974), it is possible to suggest that vanadyl in Brazilian oil has  $VO(N_4)$ ,  $VO(NS_3)$ ,  $VO(N_2S_2)$  and  $VO(N_3S_2)$  as possible environments.

After 100 h of solar irradiation the variation in the  $\Delta g_o$  value to 19.5 (Fig. 4) must be attributed to the preferential destruction of the vanadyl porphyrin complexes due to the decrease in the  $\Delta g_o$  value (Dickson and Petrakis, 1974). The uncertainty in the determination of the  $\Delta g_o$  value is  $\pm 0.1$ .

### 3.2. Organic free radicals

The EPR spectra of petroleum show resonance lines, with the most intense intermediate line corresponding to the free radical (Saraceno et al., 1961).

Organic free radicals are present in the asphaltene fraction of oils, but little is known about their molecular nature due to the multiplicity of molecular structures that causes the appearance of an unresolved single line with a width between 4 and 6 G (Scotti and Montanari, 1998).

The  $g$  parameter is sensitive to the chemical neighborhood of the unpaired electron, although the asphal-

tenes (the heavy fraction of oil) have the nature of a mixture of free radicals. These radicals are associated with a non-localized  $\pi$  system stabilized by resonance in polyaromatic centers. The  $g$  values for the free radicals of asphaltenes in some previously investigated oils range from 2.0028 to 2.0034, being higher than those of the aromatic hydrocarbon radical ions and increasing with the decrease of the aromatic fraction and the related carbon content. In a non-localized system an unpaired electron travels over the different atoms, and therefore the  $g$  value tends to increase when heteroatoms are present in the system (Montanari et al., 1998).

Requejo et al. (1992) correlated the immaturity of the bituminous material with the content of oxygen, nitrogen and sulfur. The nature of some radicals present in asphaltenes was suggested by comparison using pure model compounds. The  $g$  parameter values for the radicals in petroleum asphaltenes were found to be closest to certain types of neutral carbon and nitrogen radicals. Radicals in semiquinones show  $g$  values ranging from 2.0041 to 2.0047 (Yen et al., 1962). It was demonstrated too that all of the nitrogen of asphaltene is present in aromatic rings of the pyrrole or pyridine type and also that most of the sulfur is aromatic, especially in thiophene (Mullins, 1995). Free radicals containing sulfur have  $g \sim 2.0080$  and these values are usually higher than those found for most radicals in asphaltenes (Bielski and Gebicki, 1967).

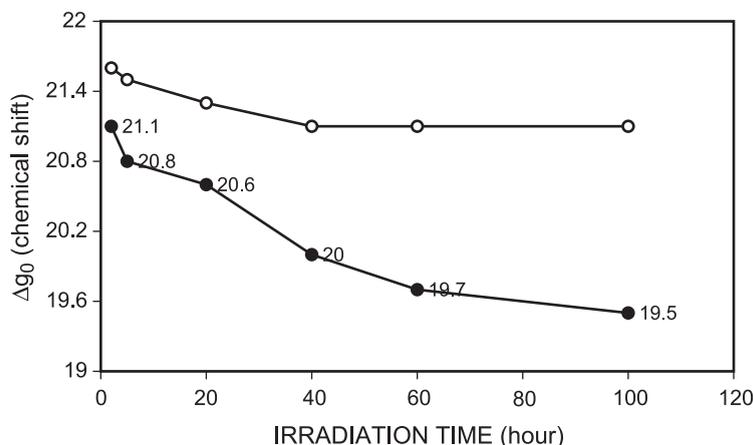


Fig. 4. Variation of the  $\Delta g$  (chemical shift) versus sunlight irradiation time. Full circles represent the irradiated samples and blank circles represent the non-irradiated samples.

The  $g$  value determined for the free radical signal in Brazilian petroleum (Campos Basin in the state of Rio de Janeiro) was  $2.0045 \pm 0.0001$  (Table 1), suggesting the presence of phenoxy radicals, i.e. radicals partially localized in aromatic systems due to the oxygen.

In a further attempt to elucidate the nature of free radicals present in petroleum asphaltenes, EPR spectra of the Brazilian oil were obtained with the addition of sodium hydroborate. The hydrogenation of the free radicals present in the oil was expected to occur in a discrete way, but the  $g$  value did not suffer alteration after the addition of  $\text{NaHB}_4$ . The line width of the free radical EPR sign in the Brazilian oil was reduced by only 1.84% with the addition of  $\text{NaHB}_4$ . These results indicate that free radicals present in the oil strongly interact with the molecular structure of the asphaltene fraction of crude oil.

In asphaltenes the hyperfine interaction is generally between the electron spin delocalized in an aromatic  $\pi$  orbital and the nuclear magnetic moments of H attached to the aromatic C. The line-width broadening of the free radical cannot be attributed unequivocally to the unresolved hyperfine structure of the EPR spectrum. In petroleum asphaltenes, the effects of the aromaticity and the different degrees of substitution on the line width and the line shape probably overlap, and different number of spins can also contribute to the line width by dipolar interaction (Scotti and Montanari, 1998).

We think that the variation in the line width is not simply due to a variety of radicals but also to the distribution of these radicals in asphaltenes. In addition, the mobility of radicals in asphaltenes is relatively low because of the high viscosity of these compounds, and consequently there will be a contribution to the line width from the anisotropic components of the  $g$  tensor (Di Mauro et al., submitted for publication).

Solar irradiation caused an increase in the line width of the signal corresponding to the free radical within the first 5 h (Fig. 3). Since we know that the photodegradation of this Brazilian petroleum under solar light begins from singlet oxygen and continues with the formation of free radicals and the destruction of aromatic components of the oil by a photochemical effect (Nicodem et al., 1998), we can say that the widening of the line was due to the increase of the

concentration of free radicals and the decrease of aromaticity in asphaltenes.

After 20 h of irradiation, narrowing of the line was detected. At the end of 100 h of irradiation the line width was reduced by 10.6%, indicating rearrangement among radicals present in the structure and probably the partial destruction of the asphaltenic fraction of the oil.

### 3.3. Unknown paramagnetic species

With the purpose of investigating the signal of the EPR spectrum of this Brazilian crude oil with a value of  $g=2.16 \pm 0.01$ , we compared the signal obtained here to similar signals described in other reports. Glinchuk et al. (1994) obtained the EPR spectrum of a ceramic ( $\text{Pb}/\text{Mg}_{1/3}\text{Nb}_{2/3}$ ) doped with iron III oxide ( $\text{Fe}_2\text{O}_3$ ) presented here in Fig. 2 (dashed line). One of the lines observed in this spectrum (magnetic field of about 3000 G) had a value of  $g \sim 2$  and was attributed to the  $-1/2 \leftrightarrow +1/2$  of  $\text{Fe}^{3+}$  transition in a crystalline field of cubic symmetry. In more recent work, Bensimon et al. (1999) obtained a very wide sign with a value of  $g \sim 2$  attributed to the hydrated  $\text{Fe}^{3+}$  species giving rise to  $\text{Fe}_2\text{O}_3$  (iron III oxide) or  $\text{FeOOH}$  (iron hydroperoxide) in fired clay. In both cases, the signals and parameters described by the cited investigators were closely similar to those obtained in the present study (Fig. 2).

Thus, the very wide line obtained in the EPR spectrum of this Brazilian crude oil (continuous line in Fig. 2) can be attributed to  $\text{Fe}^{3+}$  in  $\text{Fe}_2\text{O}_3$ , since all petroleum extracted from the marine platform can contain sand residues and traces of water incorporated into the oil. EPR spectroscopy, also utilized to investigate  $\text{Fe}^{3+}$  in porphyrin systems (Manso et al., 1999), detected this species with value of  $g \approx 6.0$  at 5 K. Guimarães et al. (2001), using EPR on the characterization of humic acids from vermicomposts, found in the spectrum a signal with  $g=6.0$  at room temperature, which was attributed to  $\text{Fe}^{3+}$  in porphyrins. Therefore, the signal of  $\text{Fe}^{3+}$  obtained in the EPR spectrum of this Brazilian crude oil does not correspond to the signal of  $\text{Fe}^{3+}$  in porphyrins. On the basis of the above facts, it is possible to state that the  $\text{Fe}^{3+}$  species observed here is not part of the molecular structure of crude oil.

#### 4. Conclusion

We may conclude that the asphaltenes of petroleum from the Campos Basin in the state of Rio de Janeiro, Brazil, contain in their asphaltene fraction: free radicals in C, N and O, and vanadyl in porphyrin and non-porphyrin (with sulfur) complexes.

Most of the free radicals present in the asphaltenes of this crude oil are imprisoned inside aromatic systems.

Solar irradiation reduces the aromaticity of petroleum degrading porphyrin complexes and destroying, at least in part, the asphaltene fraction of oil.

The  $\text{Fe}^{3+}$  signal observed is not part of the molecular structure of crude oil; it is present in  $\text{Fe}_2\text{O}_3$ .

The EPR technique proved to be useful in the characterization of the molecular structure of asphaltenes in this Brazilian oil and also revealed changes of the photochemical nature in the oil under the effect of sunlight.

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