

# Photochemical Processes and Accumulation of Solar Energy in Oil Luminophors

A. P. MAMEDOV, M. I. RUSTAMOV, R. A. DZHAFAROVA, Ch. K. SALMANOVA

*Institute of Petrochemical processes of the Azerbaijan Academy of Sciences  
30 N. Rafiev Str., 370025, Baku-AZERBAIJAN*

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Using the methods of absorption spectroscopy, luminescence and EPR there has been studied the mechanism of solar energy accumulation by high boiling products of oil refining and by luminophors prepared on their basis within wide temperature range (77-550 K). The photochemical processes with participation of all main components of oil products and luminophors have been considered.

The mechanisms of accumulation of solar energy of the studied products and luminophors have been considered. The mechanism of accumulation of solar energy of the studied products prior and above their pour points have been found to differ significantly. The light energy accumulation and its thermal luminescence have been established to occur with participation of free radicals, ions, peroxides and tetraoxides. It has been shown that low-temperature recombination luminescence takes place only by two-photon process, but photochemoluminescence-both by one photon and two-photon processes.

## Introduction

Exhaustion of combustible minerals reserves stimulated the researches in the direction of solar energy utility. Relative to this problem a number of trends were formulated by present time.

They are: the solar energy store, synchronous production of electric energy, photochemical formation of products, etc.

In many cases the necessity arises to convert the solar energy (accumulated or transformed to other kinds) to the light energy. Therefore the direct conversion of the accumulated solar energy to the light one is of interest. The luminophors are the accumulators of such kind. The existing luminophors with the above properties have the inorganic nature<sup>1</sup>, they are synthetic and of little availability.

Besides, these luminophors are incapable for prolonged store of solar energy. After cessation of the exciting light action they monotonously luminescent the accumulated energy for relatively short time interval. Duration of light energy store by organic compounds is even less. It is determined by the lifetime of their molecules triplet state. It should be noted that the prolonged store of light energy in organic compounds is possible in principle. This usually occurs at low temperature. However generated in this case the free radicals and ions often recombine prior pour point. Therefore, the store of light sum above this temperature doesn't occur.

We discovered the store of solar energy in oil luminophors (OL)<sup>2,3</sup>. This energy preserves for

prolonged time at the temperatures exceeding the pour points. It has been found out that the accumulated energy releases in the form of light energy during slight heating. Thus, the possibility arose for development of "cold" sources of light on the basis of the available OL.

We have studied the photochemical processes in OL to elucidate the mechanism of solar energy accumulation. Many photochemical processes occur extremely fast under the usual conditions. This makes difficult to elucidate the mechanism of the above processes in multicomponent OL. Taking into the consideration this fact we studied the photochemical processes in OL within wide temperature range (77-550 K) using the methods of absorption spectroscopy, luminescence and EPR.

## Procedure

Luminophors under symbolic name "Shirvanol" ("Sh1", "Sh2", "Sh3") have been prepared from high-boiling oil products by deasphaltization and partial deresination. In "Sh1", "Sh2", "Sh3" series the boiling point and molecular mass increase.

Absorption spectra were measured on spectrophotometer "Specord UV VIS". The aromatic content in "Shirvanol" was determined by the UV-spectroscopic method<sup>[4]</sup>.

The study of the integral thermostimulated luminescence (TSL), photochemiluminescence (PhChL) and chemiluminescence (ChL) was performed using diffuse reflection attachment (DRA) with elliptic mirror to spectrophotometer SF-4. The sample was placed in one focus of the mirror, in the other one was the cathode of photoelectron multiplier. The samples (with thickness 0.01-1 mm) were in special nonvacuum optic cryostat permitting the measurements within the range 77-550 K. The samples luminescence was registered by means of photoelectron multiplier (PhEM-39A or PhEM-100), direct current amplifier and electron potentiometer.

The registration of photoluminescence (PhL), TSL, PhChL and ChL spectra was carried out on photoelectric unit assembled on the basis of the crossed monochromators (SPM-2 and DMR-4<sup>5</sup>).

The samples were irradiated at 77 K by full and filtered light of mercury-discharge lamp (PRK-2) emitting in visible and UV-region of spectrum as well as by solar light for 1-30 sec.

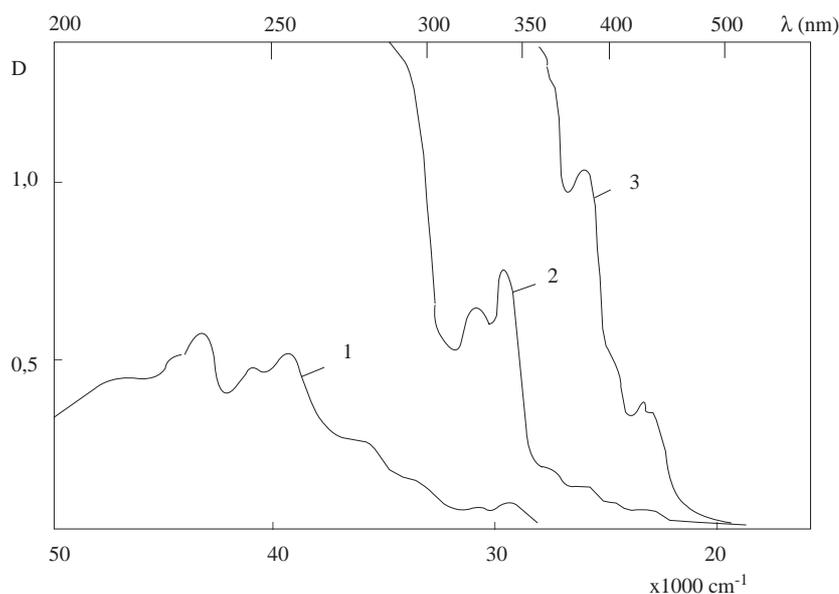
The study of the possibility for radicals formation and their nature during photoirradiation followed by heating was performed by EPR method<sup>6</sup>.

## Results and Discussion

Group composition of the aromatic hydrocarbont in OL was studied using electron absorption spectra (Fig. 1)<sup>1</sup>. The detected absorption bands in ultraviolet and visible regions of spectra are peculiar to naphthalene (226 nm), anthracene (294 nm), benzflyorene (226 nm), chrysene (270 nm), 1,2-benzanthracene and 3,4-benzaphenanthrene (295 nm), pyrene (340 nm)and perylene (435 nm). The total content of the above polycyclic aromatic hydrocarbons (PAH) determined by the method<sup>4</sup> amounts to ~40% by mass which in "Sh1", "Sh2", "Sh3" was approximately similar. However, when passing from "Sh1" to "Sh3" the relative content of low-molecular PAH decreased, that of high-molecular ones increased. The remaining components in OL are naphthene-paraffin hydrocarbon (55%), resins and olefines (about 5% by weight).

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<sup>1</sup> Absorption spectra of the luminophors studied are not differed gualitatively therefore the spectrum of one of them ("Sh3") is given in Fig. 1



**Figure 1.** Absorption spectra of oil luminophor “Sh” in isooctane measured at different thickness of absorbing layer (1,2,3)

In PhL spectrum of OL one intensive band is shown inherent to the relatively high-molecular PAH. The maxima of these bands are located at 495,517,545 nm, respectively, for “Sh1”, “Sh2” “Sh3”. The position of PhL band is independent of the exciting light frequency in spite of the presence of different PAH in luminophors. This indicates the “cascade” transfer of energy from low-molecular to high-molecular PAH<sup>2</sup>.

In linear heating of photoirradiated at 77 K OL a number of luminescence peaks are observed, the maxima of which are located both lower and higher than their pour points (Fig.2a).

The low-temperature peaks are located at 108,165 and 198 K, the high-molecular ones-at 323,367,403 and 510 K.

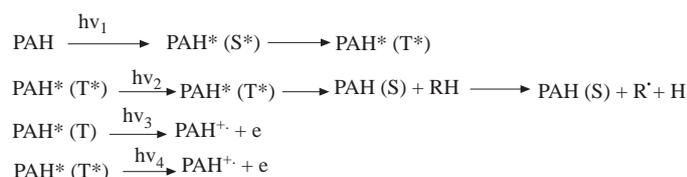
During not long (1-5 sec) photoirradiation the low-temperature peaks and the most high-temperature peak<sup>2</sup> are observed, during long (15-30 sec) photoirradiation the decrease of their intensity and amplification of the other peaks occur.

The peaks are usually observed at temperatures lower or equal to the pour points of substances. Therefore their detection at temperature higher than the OL pour points (270-295K) arose the great interest.

In most cases TSL was studied in organic compounds subjected to the action of high-energy radiation ( $\gamma$  and x-rays, quick electrons). The ideas on origin of TSL peaks are mainly referred to these irradiation conditions. However, the effective TSL in OL is observed also after photoirradiation in long-wave ultra-violet and short-wave visible regions of spectrum. The energy of light quantum in the above regions is not sufficient for decomposition and ionization of the molecules of organic compounds in OL. Therefore, it should be assumed that TSL occurs as a result of two-photon processes.<sup>6,7</sup>

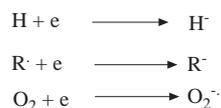
The processes of two-photon adsorption, decomposition and ionization of molecules at 77K with participation of PAH in OL may be presented as follows:

<sup>2</sup>Peak at 510 K is also observed during heating of the OL, not subjected to the action of photoirradiation. Therefore the specific mechanism of the origination of this peak assigned to the chemiluminescence is not considered in the present work.



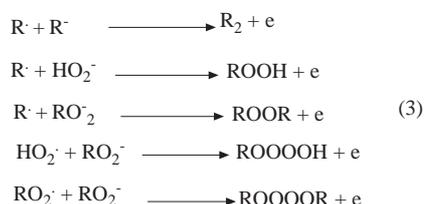
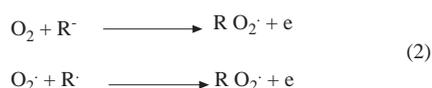
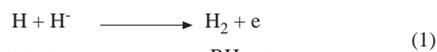
where S, S\* and T, T\* -the basic and excited singlet and triplet states of PAH molecules; RH-molecules of NPH, e-electron.

Due to relatively large affinity of the radicals formed and the dissolved in OL molecular oxygen O<sub>2</sub> with electron the formation of their ions takes place, too:



During the heating of photoirradiated at 77 K samples the recombination of the electrons formed, free radicals and ions takes place. The formation of radicals H, R, HO<sub>2</sub>, RO<sub>2</sub> and their destruction in the TSL peaks region were shown by EPR method<sup>8,9</sup>. However, the recombination of free radicals has been found not to be accompanied by luminescence. This was proved by the formation of such radicals in the compounds subjected at low temperature to mechanic destruction and heating in TSL peaks region<sup>10</sup>.

The experiments on irradiation by visible light of OL preirradiated by UV light at 77K showed that in this case in spite of the radicals concentration preservation TSL is absent or it is strongly weakened. This in accordance with<sup>11</sup> evidences that TSL of the systems studied is due to ionic processes. Considering these fact as well as the temperature region of radicals destruction, it should be assumed that TSL peaks formation at temperatures 108,165 and 198 K is connected with the following reactions<sup>1-3</sup>, respectively:

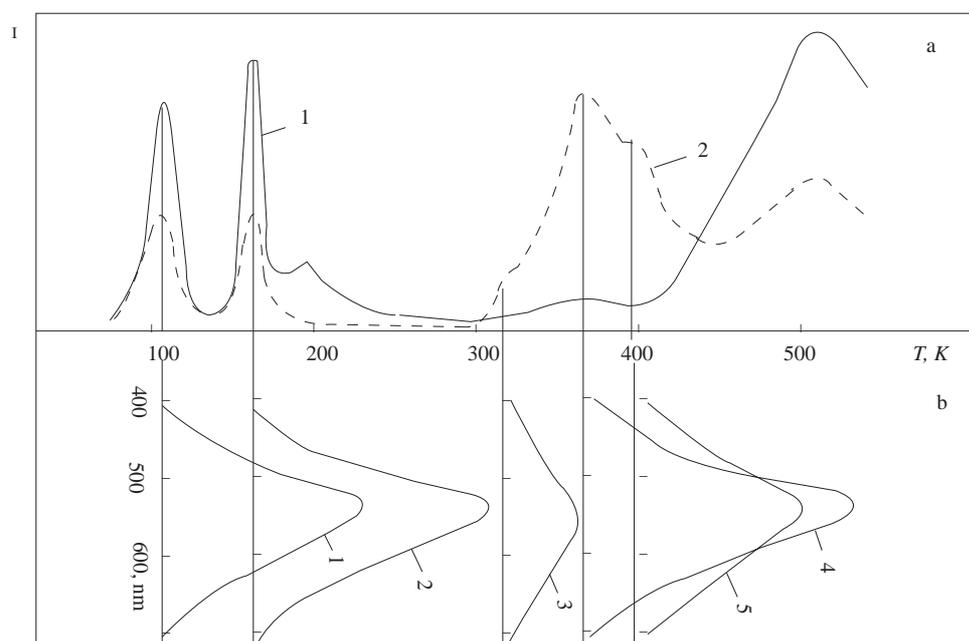


In the above reactions taking place during heating with ions and radicals participation the electron release occurs. The luminescence in the region of all observed TSL peaks has the similar spectral composition (Fig.2b) and corresponds to Phl spectrum. This fact indicates that the final stage of the reaction (1-3), leading to TSL peaks formation at low temperatures, is the reaction:



During heating to the pour points of luminophors “Sh1”, “Sh2”, “Sh3” (270-295 K) all radicals and ions generated by photoirradiation at 77K are destroyed as a result of their recombination, and the stable molecules are formed. The formation of molecular hydrogen and hydrocarbons RH (methane, ethane, propane, etc) in the photoirradiated OL was confirmed by the method of chromatography<sup>11,12</sup>, and that of peroxides -by colorimetry method<sup>13</sup>.

The great interest caused the appearance of a number luminescence peaks (at 323,367 and 403 K) during the heating of photoirradiated OL, located at temperature higher than pour point since prior these temperatures the recombination of the induced radicals and ions occurs. The necessary condition for the detected peaks rise is the presence of molecular oxygen in OL. Therefore the maxima of luminescence at 323, 367 and 403 K (Fig.2a) should be referred to PhChL.



**Figure 2.** a) Curves of TSL, PhKhL and ChL of oil luminophor: 1- after photoirradiation for (1-5) sec. 2- after photoirradiation for (15-30) sec. b) Spectral composition of TSL (1,2) and PhKhL (3,4,5).

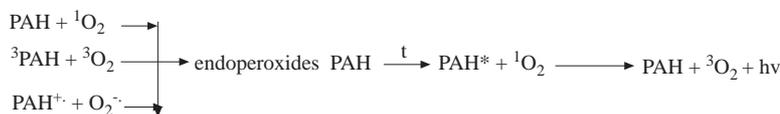
PhChL is observed during heating (higher than 300K) of photoirradiated OL within wide temperature range (77-300K). The range of exciting rays energies is also wide and covers the region of x-rays, ultraviolet and short-wave part of the visible spectrum. The intensive PhChL arises also in OL exciting by he undecomposed solar light. This evidences the efficient accumulation of solar energy followed by its release in the form of light quanta during heating.

The intensity of all PhKhL maxima increases with the increase of PhL quantum yield and its spectrum is similar with PhL spectrum. (Fig.2b). It gives grounds to affirm that apart from OL components nature and PhKhL mechanism the final stage of luminescence is the formation of the excited states of PAH molecules. The relation of intensities of PhKhL maxima depends on the nature, component content and origin of OL.

In accordance with three main classes of hydrocarbons (PAH, NPh and olefines) in oil and the detected PhKhL maxima (323, 367 and 403K) three mechanisms of their formation have been considered. These mechanisms are connected with the thermal decomposition at temperatures higher than 300K of relatively low stable proxides<sup>14</sup> and tetraoxides of the above hydrocarbons formed during OL photoirradiation prior this temperature.

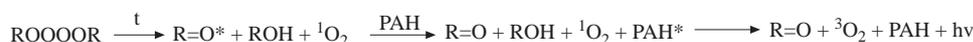
It is known that a number of PAH form endoperoxides with molecular oxygen which emit the light quanta in thermal decomposition<sup>15</sup>.

The possible variants of formation of the above endoperoxides and radiative deactivation of the formed during their decomposition of the excited molecules are summarised as follows:

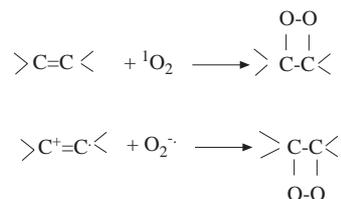


OL photoirradiated at low temperature as a result of the reactions (2,3) during heating may form peroxides and tetraoxides belonging to napheno-paraphinic hydrocarbons and olefines. The peroxides and tetraoxides are formed at rather more rate in OL photoirradiated at temperatures higher than pour point.

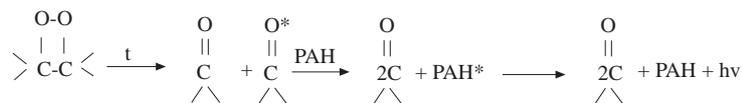
The decay both of peroxides and tetraoxides during heating is accompanied by the formation of one of the PhKhL maxima. This process exemplified takes place as follows:



Olefines in OL upon photoirradiation in the reactions with molecular oxygen, as PAH, may form the cyclic peroxides (dioxetanes):



It has been established that in heating dioxetanes are decomposed into carbonyl-containing compounds in basic and excited state<sup>14</sup>, which interacting with the molecules of activators (PAH) emit the luminescence characteristic of the latter:



Thus, at temperatures higher than the OL pour points liberation of the accumulated solar energy occurs in the process of thermal decay of PAH endoperoxides, NPH peroxides and tetraoxides and olefine dioxetanes irrespective of the nature of these peroxides and tetraoxides, the final stage of their decay is the transfer of the liberated energy in this case to PAH the luminescence of which is observed in PhKhL spectra.

Irradiation of "Shirvanols" by monochromatic light in the whole region of absorption bands showed that TSL is absent and only maxima of PhKhL are observed. It gives ground to consider that TSL occurs by two-photon process and PhKhL may take place both by one-photon and two-photon process.

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