*Petroleum and Coal, Vol. 43, **1**, 35–40*

DETERMINATION OF STABILITY OF MINERAL OILS, CRUDE OILS AND WAXES BY CHEMILUMINESCENCE

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Abstract. *Chemiluminescence (CL) method based on measurements of ultraweak light emitted from the oxidized sites of the material proves to be useful test in assessing the service life prediction of mineral oils, crude oils and various paraffins or their mixtures. The results of CL evaluation of thermo and/or photostability of waxes from different crude oils, of the wax prepared from one crude oil modified to the different extent by hydrofinishing as well as of some mineral oils are presented. Characteristics resulting from CL measurements are compared with those obtained by more common tests.*

Key words: *waxes, thermo and photooxidative stability, chemiluminescence*

Introduction

Photo and thermal stability of crude oil products (fuel oils, vacuum distillates, waxes, tars) determines their use and applicability in crude oil industry. Standard analytical procedures, which are used for evaluation of the oxidizability of these materials do not yield an integral view on the process and development of the new sophisticated approaches is therefore necessary.

Chemiluminescence (CL) method belongs to those which is relatively new but very promising technique of characterization of the oxidizability of crude oil products. It is well known that the oxidation of organic materials is usually accompanied by the emission of light in the visible spectral region which originates from some reaction product being formed in an excited state. McCapra and Perring [1] formulated a general rule according to which CL reaction should involve a rapid exothermic step such as fragmentations, rearrangements and electron transfer which releases enough energy for excitation

$$h\nu = E_a - \Delta H$$

where E_a is the activation energy, ΔH is the heat of reaction and hv is the energy of photon. Minimum energy required is 300–350 kJ/mol. Most of the scientists [2] believe that the reaction pathway leading to the chemiluminescence reaction is the self recombination of secondary peroxy radicals:

$$R\text{-}CXH\text{-}OO^{\cdot} + ROO^{\cdot} \rightarrow R\text{-}C(X){=}O^{*} + ROH + O_2 \qquad [1]$$

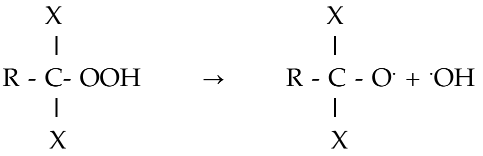
where X is alkyl or H.

The gain of energy from this reaction is higher than 400 kJ/mol. Ketone is formed in an excited triplet state; emitted light is phosphorescence. Because of the spin conservation rule, oxygen should be formed in the excited singlet state. Both particles can thus emit light when passing to their ground state. This mechanism was considered by the Russian groups around Shlyapintokh [3] and Vassil'ev [4] for the kinetic scheme describing CL at oxidation of low molecular hydrocarbons.

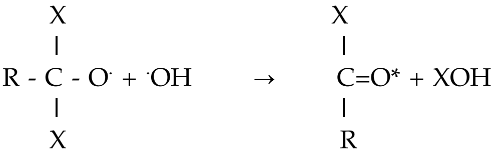
The second reaction which may be the possible source of CL is decomposition of hydroperoxide [5].

$$R\text{-}CX_2OOH \rightarrow \underset{\underset{\displaystyle O^{*}}{||}}{R\text{-}CX} + XOH \qquad [\ 2]$$

This reaction should take place as the sequence of two steps:



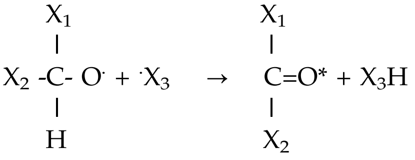
$$R - \underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle X}{|}}{C}} - OOH \quad \rightarrow \quad R - \underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle X}{|}}{C}} - O^{\cdot} + {}^{\cdot}OH \qquad [2a]$$



$$R - \underset{\underset{\displaystyle X}{|}}{\overset{\overset{\displaystyle X}{|}}{C}} - O^{\cdot} + {}^{\cdot}OH \quad \rightarrow \quad \underset{\underset{\displaystyle R}{|}}{\overset{\overset{\displaystyle X}{|}}{C}}{=}O^{*} + XOH \qquad [2b\ ]$$

and E_a- ΔH = –315 kJ/mol

Metathesis reaction of alkoxy and alkyl radicals was also considered as a potential source of the formation of excited particles [6]



$$X_2 \text{-}\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle X_1}{|}}{C}}\text{-}\ O^{\cdot} + {}^{\cdot}X_3 \quad \rightarrow \quad \underset{\underset{\displaystyle X_2}{|}}{\overset{\overset{\displaystyle X_1}{|}}{C}}{=}O^{*} + X_3H \qquad [3]$$

E_a - ΔH = –374kJ/mol

Experimentally measured value, the intensity of the light emission, will be proportional to the rate of elementary reaction providing excited molecules in the oxidized hydrocarbon.

In the case of the validity of the scheme [1] the intensity will be given by the equation

$$I = \delta\, \eta\, k\, [\, RO_2^{\bullet}]^2 \qquad [4]$$

where	δ	is geometry factor
	η	quantum yield of chemiluminescence
	k	rate constant of self-recombination of peroxy radicals
	$[RO_2^{\cdot}]$	concentration of peroxy radicals

Typical quantum yield of the CL emission during oxidation of hydrocarbon is 10^{-9} photons per 1 reacted molecule.

In the last decade, chemiluminescence has been applied to a higher extent for the study of oxidation of high molecular hydrocarbons, mainly polyolefins, polyamides, etc. [7–11] . Probably the most practical output of CL technique is the estimation of antioxidative efficiency of inhibitors (InH) in the oxidation of hydrocarbons. If the molecules InH reduce the stationary concentration of peroxy radicals or hydroperoxides, then the CL intensity is reduced proportionally to the reactivity and concentration of the inhibitor. We have proved that the identical sequence of reactivity of substituted alkylphenols in polypropylene was obtained for both, the CL and oxygen-absorbtion methods when measuring the induction period of the increase of chemiluminescence or of the amount of oxygen absorbed. The different inhibitors and stabilising mixtures can thus be evaluated and the coincidence with other tests should be verified. Papers devoted to this topic are, however, very scarce [12–15].

This contribution is aimed at the description of the possibilities and potential application of chemiluminescence method for characterization of thermo- and/or photo stability of the products from crude oils from several sources (mostly in India and in Russia), especially of waxes and oils.

Experimental

Materials. Waxes were prepared from crude oils of different origin (India-Bombay High, Japan and Germany); some of their physical properties are summarised in the Table 1, while the distribution of carbon atoms may be seen in Figure 1.

Table 1. Some physical properties of waxes obtained from 3 different sources

	Germany	Japan	India
d_4^{20}	0.8202	0.8104	0.8285
mpt, °C (cooling curve)	60.8	61.7	64.0
Oil content, wt%	0.35	0.15	0.30
Refractive index, 70 °C	1.4348	1.4339	1.4438
Kin. Viscosity cst, 100 °C	4.70	4.50	4.51
Hydrocarbon type analysis (Mass, %)			
0- ring	84.4	97.9	96.0
1- ring	12.3	1.8	3.7
2- ring	1.0	0.1	0.1
3-4 ring	1.0	0.1	0.0
mono aromatics	1.5	0.1	0.2
Av. Carbon No. (G.C.)	30	29.5	31.0
CH_3/CH_2 ratio (IR)	0.1934	0.2451	0.1904

Some waxes prepared in Slovnaft, Slovak Republic from vacuum oil fraction of Siberian crude oil were hydrofinished at high pressure (Table 2). Their physical properties are given in Table 3.

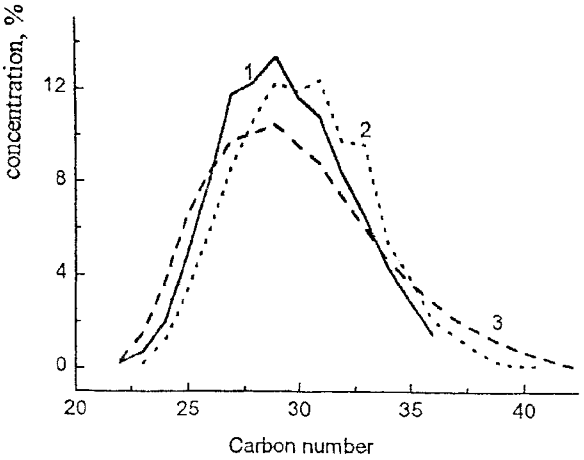


Figure 1. Carbon number distribution of n-alkanes present in waxes.
curve: 1 – wax from Japan, 2 – from India, 3 – from Germany

The initial material for preparation of lubricants are base stocks. Two oils from high boiling fractions (370 °C and above) of crude oil, denoted as L83 and L85 were used. L83 is light neutral while L85 is heavy neutral according to the refinery process. The samples LO83 and LO85 are thermally preoxidized samples L83 and L85.

Mineral oil was used for the demonstration of the effect of inhibitors and peroxides decomposer on the thermo-oxidation stability.

Equipment. Three instruments have been used.

1. Spectrometer PU SNK 7M of Russian production with an analogous output, working with samples in glassy ampoules, monitoring the light emission from the side of the ampoule. The mass of the samples was 5.5 g, the stream of gas (oxygen or nitrogen) over the material was 100 ml/min. The intensity of emitted light is given in relative units.

1 rel. u. corresponds to the electric current 3.6 x 10^{-13} amperes at the resistance 1x 10^{11}ohms.

2. Photon counting luminometer Biolumat (B 9501) fy Berthold, Germany, was adopted for the measurements at temperatures till 210 °C. The heating block of the apparatus was replaced by the calorimetric head.

3. Photon counting luminometer Lumipol produced in 1997 at the Polymer Institute of the Slovak Academy of Science, Bratislava. It was designed as prototype of an extremely sensitive equipment having the versatile and reliable operational capacity.

The sample used for experiments performed on apparatus 2 and 3 of the mass from a few milligrams to 50–60 mg is put on an aluminium pan and electrically heated; the

Table 2. Procedures of preparation of waxes

Sample	Procedure
No 1	Wax of grade g = 58/60, isolated from hydrocracked distilled oil on bifunctional catalyst at 420 °C, pressure (p) 140 bars, volume velocity, v.v. = 0.57 h^{-1} , ratio H_2/raw material, r = 650 dm^3/dm^3
No 2	High quality Russian acid refined wax, g = 54/56
No 3	Wax of g = 58/60, isolated from hydrocracked distilled (as wax sample 1) oil on catalyst NiW/Al_2O_3 at 378 °C, p = 120 bar, v.v. = 0.80 h^{-1}, r = 500 dm^3/dm^3
No 4	Wax having g = 58/60 was isolated from hydrocracked mixture of two oils in the ratio 1:1, other conditions were the same as for the sample 1.
No 5	Hydrofinished raw wax, g = 58/60, at 300 °C , p = 50 bar, v.v. = 0.4 h^{-1}, r = 1000 dm^3/dm^3
No 6	Raw wax , g = 54/56, isolated from oil distillate by 4-steps dewaxation

Table 3. Some physical properties of slovak waxes

sample No	melting point °C	content of oil % of wt	colour[1]		light stability	
			r	y	uv[2] $\Delta r/5$	daylight[3] $\Delta r/21$
1	59.6	0.5	0.1	0.2	0.2	0.2
2	54.6	0.75	0.0	0.3	0.3	0.3
3	60.1	0.6	0.1	0.8	0.3	0.3
4	58.0	1.7	0.5	2.0	0.8	0.5
5	60.2	0.4	0.2	1.0	0.8	1.5
6	56.9	1.2	1.9	5.9	2.0	2.8

1. Lovinbond method, measuring cell 2", in red and yellow region
2. UV light, deterioration of colour after 5 hours,
3. Dissipated day light, after 2 hours

intensity of CL is given in counts/s (Hz) as an average value at a certain time interval (mostly 10 s) at constant temperature (isothermal mode) or at increasing temperature with the constant rate of heating 5°/min. (dynamic mode – RAMP experiments).

Results and Discussion

Comparison of thermooxidation stability of waxes of different origin. Three waxes were oxidised in O_2 atmosphere at 120 °C and CL was registered (Figure 2).

CL curves show two maxima. The first one A of lower intensity is observed immediately after the heating of the sample to the measuring temperature. It was shown on low-molecular models and mainly on macromolecular substances as isotactic polypropylene, etc. that the origin of this first increase corresponds to the inherently present hydroperoxides and peroxy-structures and to the other easily oxidised impurities formed during preparation, processing and storage of the material. Such structures are usually thermally unstable and decompose to free radicals. In the later stage of oxidation after some apparent induction time, the CL increases in an autoaccelerating manner to the second maximum B indicating a significant consumption of oxidizable sites in the system. It is of interest, that the length of the induction period and the intensity corresponding to this second maximum are directly proportional to the magnitude of the first maximum. Such correlation should be of significance in estimation of oxidizability of materials and enables to replace the time consuming measurements of CL at lower temperature by the tests in which only the beginning of oxidation is traced. It is worth of knowing that under such conditions the most of the analytical methods used, e.g. spectral methods, are not sensitive enough to register any change. It was found by thermogravimetry that the weight loss at the heating of samples of waxes at 120 °C for 100 000 seconds was very low, namely 0.05% for India crude wax, 0.085% for Japan wax and 0.10% for Germany wax. On the other hand, by CL the differences among individual samples due to O_2 attack are very essential.

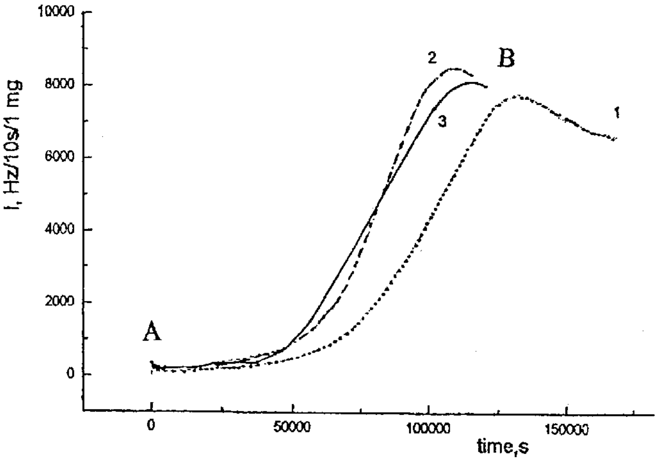


Figure 2. Dependence of CL intensity on time for the oxidation of waxes at 120 °C in O_2; CL instrument 3, m_o = 20 mg; curve 1 – wax from India, 2 – from Japan, 3 – from Germany

Analysis of the hydrocarbon content shows on the similarity between India and Japan wax (Table 1) while induction periods determined by chemiluminescence are 50 000 s for Germany wax, 55 000 s for Japanese and 69 000 s for India wax, respectively, which corresponds quite well to the Figure 1 where the maximum on the distribution of carbon atoms is shifted more to the right for India wax. The effect of very high content of linear – CH_2 – structures in Japan wax , which should reflect a good thermooxidative stability is decreased by the higher content of tertiary carbons (see last row of Table 1). They are, in fact, much more sensitive to the oxygen attack than – CH_2 – moieties.

The effect of pressure hydrogenation on the stability of waxes. A plot of CL intensity on time for individual waxes at the isothermal measurement at 120 °C carried out on spectrometer 1 is seen in the Figure 3. The intensity reaches a maximum value (Imax) and then it decreases to some stationary level (I_{stat}) which remains constant till the end of inhibition period. Similar shape of intensity curves was obtained also at 150 °C.

At lower temperature (80 °C), the maximum is less

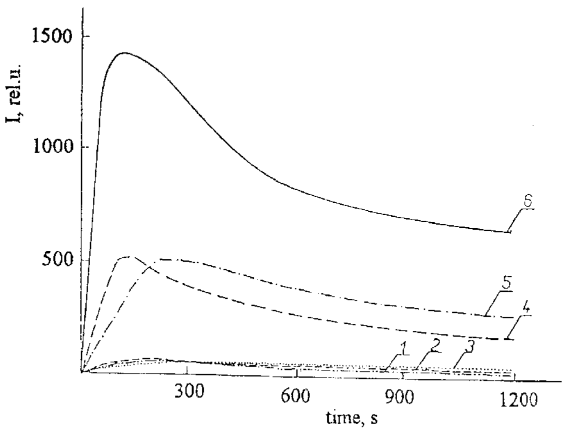


Figure 3. The courses of CL intensity with time at 120 °C in O_2. (For curve numbering see Table 3).

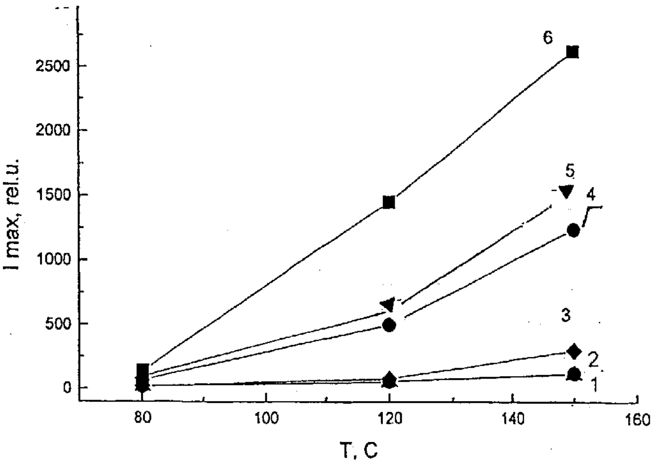


Figure 4. The increase of the maximum values of CL intensity (I_{max}) with the temperature in the oxygen atmosphere. (CL instrument 1)(For numbering of curves see Table 3)

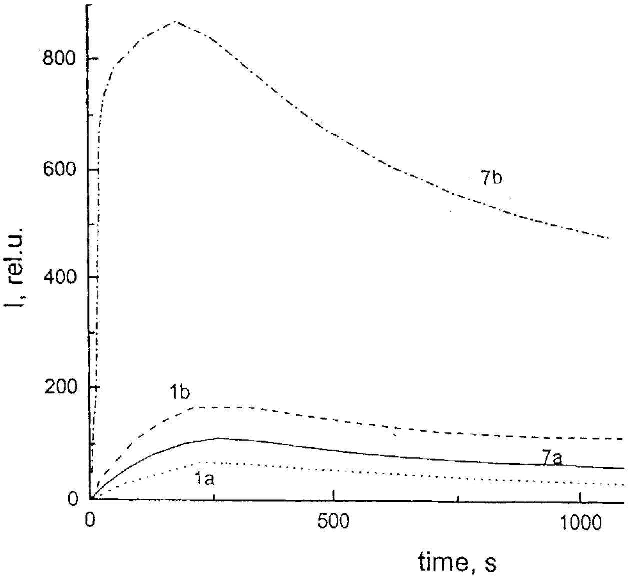


Figure 5. Comparison of the dependences of CL intensity on time at 120 °C in O_2 for samples before (a) and after 3 hours of irradiation by UV light (b). Sample 1 – see Table 2, Sample 7 – raw wax of grade 45/56 hydrofinished at 320 °C, pressure 50 bars, r = 1000 dm^3/dm^3.

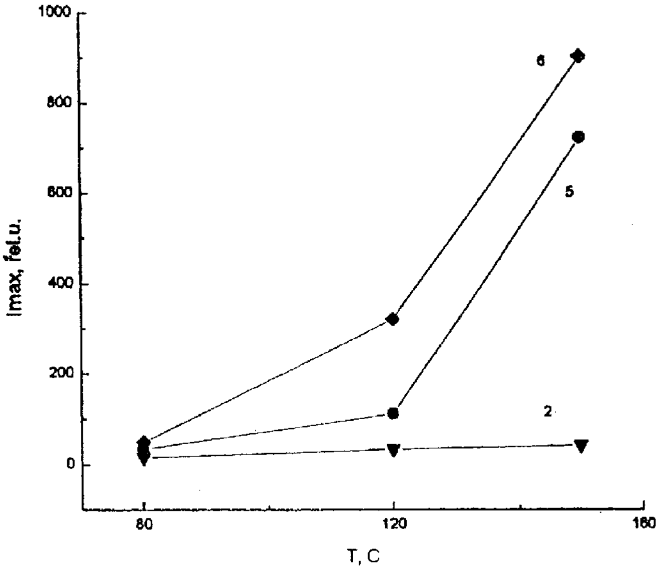


Figure 6. The changes of maximum values of CL intensity (I_{max}) with the temperature in nitrogen atmosphere for samples of raw wax (No 6), hydrofinished wax (No 5) and high quality wax (No 2) (see Table 2).

distinct and the difference between I_{max} and the stationary level of intensity is small. Raw paraffin (sample 6) is an exception. According to the values I_{max} (Figure 4) the sequence of samples having increasing thermooxidation stability corresponds to the degree of hydrocarbons refining. It decreases from the sample 1 to the sample 6.

CL intensity at the given experimental conditions differentiates well the highly refined waxes (samples 1, 2 and 3) with Imax 150–350 rel.u. from less refined (4 and 5) (I_{max} being 1200 – 1400 rel.u.) and from raw wax with I_{max} > 2500 rel.u. (The values are valid for temperature of the experiment T = 150 °C).

Irradiation of the waxes by UV light results in an increase of CL emission. An example of the effect of UV light may be seen in the Figure 5.

The effect of light is less pronounced for sample 1, which thermooxidation stability is high as well. By heating or by irradiation of waxes, the concentration of peroxy radicals in the sample increases and consequently the higher level of CL intensity may be obtained. Photostable wax has the coefficient of r/5days = 0.4 in maximum and r/21 days = 0.3 (see Table 3). At the same time, these samples perform good thermooxidation stability, which may be seen on spectral characteristics from the deterioration of the colour after heating of sample 7 days at 150 °C in the presence of Fe_2O_3.

Similar parameters may follow from the maximal CL intensities. For hydrofinished paraffins in the atmosphere of O_2 at 150 °C the upper limit for photostable wax was 500 rel.u. and for the wax of low photostability 1500 rel.u.

Certain levels CL intensity can be seen even during the heating of waxes in nitrogen atmosphere. The maximum CL values for 2 wax samples are depicted in Figure 6.

The emission is due to peroxy structures formed during the technological procedure of wax production which are more or less destroyed by refining.

The values of CL intensity obtained by heating of waxes

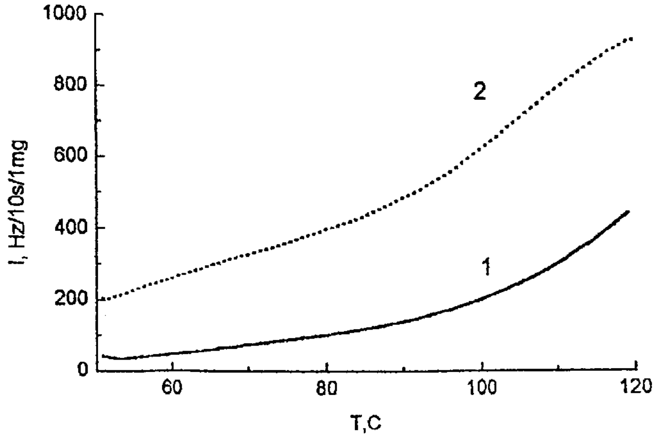


Figure 7. Dependence of CL intensity on temperature for light (1) and heavy (2) base stock in atmosphere of O_2. Temperature interval 50–120 °C, rate of heating : 5°/min; (CL apparatus 3).

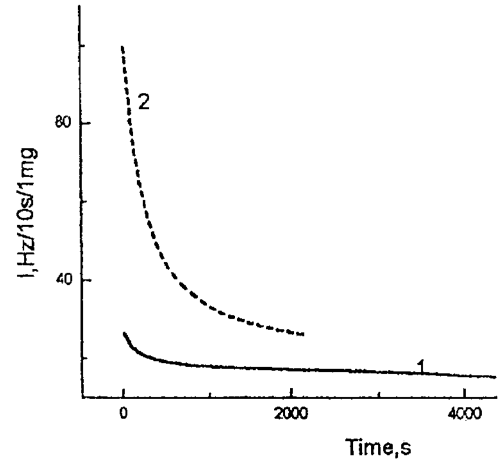


Figure 8. Isothermal CL intensity during the heating of light (1) and heavy (2) base stock at 120 °C in O_2 ; (CL apparatus 2).

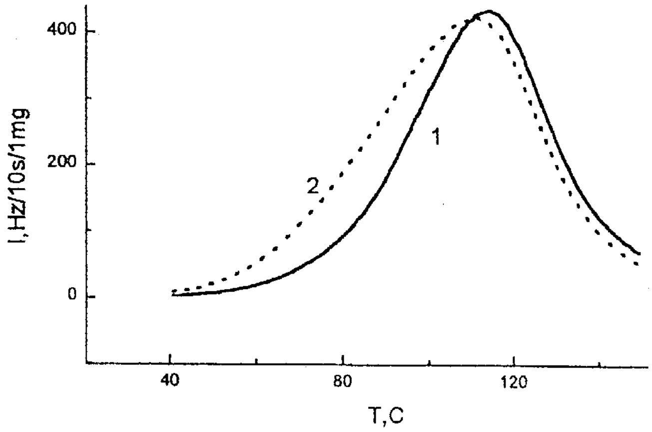


Figure 9. Comparison of the dynamic CL curves in the temperature interval 50–150 °C in N_2 for preoxidised base stocks. curve 1. LO83, curve 2. LO85; (CL instrument 3).

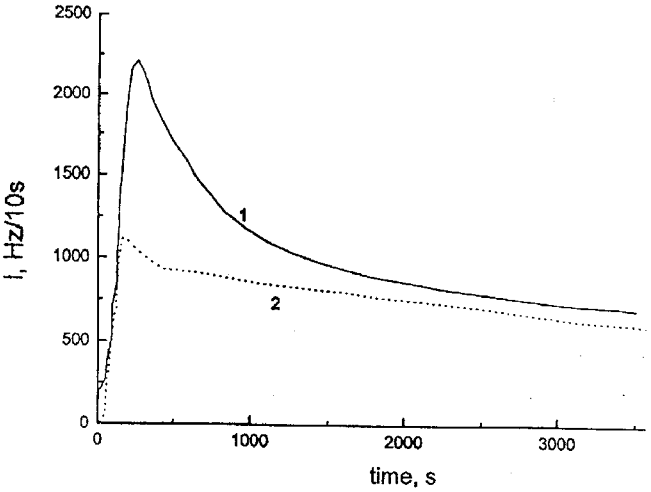


Figure 10. Dependence of CL intensity on time for oxidation of oil - O-22 at 120 °C in oxygen before (1) and after (2) the treatment with hydroperoxide decomposer. (CL instrument 2)

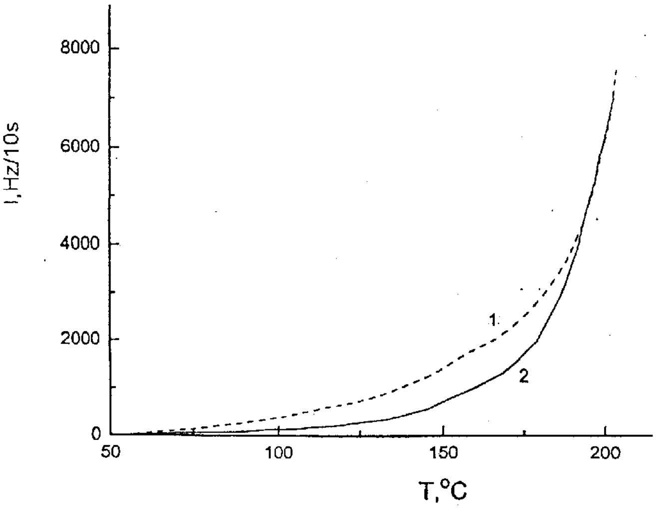


Figure 11. The effect of hydroperoxides' decomposer on the CL of the oil O-22 oxidation under dynamic mode. Curve 1: pure oil, curve 2: 'oil after the treatment.

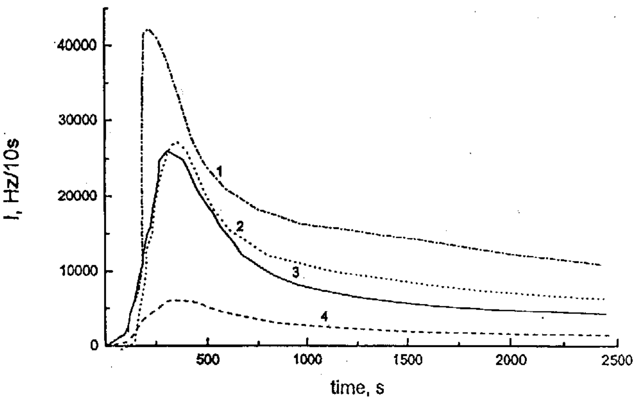


Figure 12. Time dependence of Cl intensity for oxidation of mineral oil O-935 pure (curve 1) and of the oil stabilized with $2x10^{-2}$mol/dm^3 of 2,6-ditert.butyl- 4-methyl phenol (2), Irganox 1076 (3) and N-phenyl-p-phenylene diamine (4) at 150 °C in oxygen (CL instrument 1).

in an inert atmosphere can also estimate their quality and purity.

CL of oxidation of base stocks and mineral oils. Oxidation of two base stocks was followed by dynamic CL (Figure 7) as well as by isothermal CL technique (Figure 8).

It may be shown that the sample of heavy base stock is oxidised more easily. The parameter enabling the comparison of both samples is the surface below the intensity curve. This is proportional to the concentration of excited molecules which are formed during the experiment. As the ratio of these surfaces for oxidation of L85 and L83 is around 3, a conclusion may be adopted that about 3 times higher content of potential initiators of oxidation is present in heavy base stock. Such conclusion is confirmed also by isothermal runs (Figure 8). For preoxidised samples of stocks (LO83 and LO85), the CL method may yield an valuable information about the kinetics of the decomposition of peroxidised structures formed in oxidation (Figure 9) of the system.

We have to underline, that samples after long term thermooxidative treatment are heavily coloured to dark brown and will absorb a great deal of emitted light except for photons emitted from a thin zone close to the surface. Nevertheless, the shape of CL curve does not seem to be distorted essentially. The temperature of the maximum rate of decomposition of peroxidic structures occurs at 110 °C. The difference in the concentration of peroxidic structures is not very pronounced. By iodometric titration we obtained the following values of concentrations of peroxy structures
preoxidised heavy base stock (LO85) : 1×10^{-2} mol/kg
light base stock (LO83) : 7×10^{-3} mol/kg

The ratio of integrated curves of Fig 9 is 25568/18615 (1.38) the value being in a good accordance with the ratio of content of peroxidic compounds in the samples.

CL method may be reliably used for the determination of stabilizing efficiency of various stabilising system. We present here one example of such application.

Two mineral oils from the industrial production (O-22 and O-935) were oxidized at the temperature 120 °C as well as at the increasing temperature in the interval from 50° to 200 °C and the CL intensity was registered (Figure 10 and 11, curves 1). The second set of measurements was performed after 10 minutes of the oil treatment with a decomposer of hydroperoxides (clay mineral) at 120 °C. The improved stability of the oil can be seen by comparing of curves 1 and 2 of the above Figures.

Such simple treatment improved the thermooxidative resistance of the oil distinctly; the temperature of the beginning of oxidation was shifted to the higher values for almost 50 °C. The last Figure depicts the effect of 3 different antioxidants (two phenols and one aromatic amine) on the chemiluminescence dependence on time for the oxidation of the mineral oil O-935 at 150 °C.

The decrease of the CL intensity curves for the stabilized sample which is a measure of the effectiveness of antioxidants is more pronounced for an aromatic amine. Phenols used are less effective.

Conclusions

a/ Chemiluminescence technique can be used for rapid and comfortable estimation of the oxidative stability of a wide range of organic compounds,

b/ It is a suitable method for comparison of antioxidative efficiency of different inhibitors and decomposers of hydroperoxides,

c/ The method is extremely sensitive and allow studies under relatively low temperatures, more closely to the real conditions,

d/ Small amount of samples are required for each test.

Acknowledgement

This paper was supported by grants No 2/7130/00 and 2/1127/01 of the Grant Agency VEGA of the Slovak Republic. Samples of Slovak waxes were kindly supplied by VURUP, Bratislava. The authors also acknowledge the help of Prof. V.Macho from Slovak Technical University, Bratislava, who provided us with some samples of mineral oils.

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