Eutectic Alloys in Sulfur-Based Rubber Vulcanizing Systems and Related Problems

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ABSTRACT: An analysis of phase diagrams for alloys of components of sulfur-based rubber-vulcanizing systems permitted the calculation of weight ratios and melting temperatures of their eutectic alloys. From Mukhutdinov studies it is known that the formation of a simple eutectic alloy of chemical additives makes possible the reduction of their concentration in sulfur-based vulcanizing systems without decreasing, or even while increasing, their effectiveness. However, to create eutectic alloys, these additives should be in adequate concentration and dispersed within rubber compounds. Therefore, as a successive step of this investigation, zinc stearate dispersion was determined using the radioisotopic method. For this purpose a typical tread-rubber compound with a radioactive zinc stearate (containing ^{65}Zn) was prepared, and then the γ radiation intensity from the rubber samples was measured to determine the zinc stearate dispersion. There wasn't a uniform distribution of this additive within the rubber compound. It was found that zinc stearate doesn't bloom from the compound at a 3% concentration. Also, oil dispersion in different sulfur granules was determined by an ultrasensitive CCD camera. It had been employed to monitor the surface intensity of an ultraweak chemiluminescence of oil in sulfur subjected to oxidative deterioration stimulated by ozonization. The tested samples of soluble sulfur were oiled uniformly, but the polymeric sulfur samples were not. Thus, the probability of creating eutectic alloys with such kinds of sulfur during rubber compounding and processing depends on their local concentration of oil. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1929–1941, 2001

Key words: eutectic alloys; curatives; uniformity; oiled sulfur; stearic acid; zinc stearate; dispersion; radioisotopic method; chemiluminescence; 2-D single-photon-counting imaging

INTRODUCTION

Rubber compounds containing raw rubbers that differ greatly in viscosity or/and polarity and are

filled with carbon black and/or silica may increase compatibility problems, resulting in poor dispersion of many ingredients. It is known that curatives could contain zinc oxide + stearic acid + sulfur or, alternatively, zinc stearate + sulfur. The uniform distribution of the components of rubber compounds within the polymer matrix during processing depends on their amount and their physical state (solid or liquid). On the other hand, the melting temperature of solids depends on their initial properties and whether they are in-

dividual components or, under some conditions, eutectic alloys. Taking all this into consideration, the aim of this work was to study conditions for the creation of eutectic alloys of these ingredients, an important investigation because the formation in binary and complex systems of simple eutectic alloys of chemical additives makes it possible both to obtain more uniform rubber compounds and to reduce their concentrations in sulfur-based vulcanizing systems without a decrease or even with an increase in effectiveness.[1–5] However, to ensure that the optimal properties are used in sulfur-based curing system, chemical additives should be dispersed well in elastomers. Zinc stearate, as it is a saturated aliphatic zinc soap, is insoluble in rubber, and the estimation of its dispersion is very important. The use of sulfur in the form of pastes (in mineral oils) of different consistencies delivered as granules could facilitate dispersion of the components in a rubber compound as a result of their wetting by the oil and could prevent the formation of dust during transportation and rubber compounding. However, the preparation and application of viscous pastes is associated with technological difficulties. At the same time, it has been observed that oiled sulfur granules delivered by some producers have a nonuniform consistency. Oil dispersion in sulfur determines the probability of the creation of eutectic alloys of it with the other ingredients of rubber compounds during mixing and processing. Therefore, an evaluation of the degree of oil dispersion was the analytical problem tackled in this study. Additives should be in adequate concentration and dispersed within rubber compounds to create eutectic alloys. Therefore, as a successive step of this investigation, zinc stearate dispersion was determined using the radioisotopic method. For this purpose the typical tread-rubber compound with the radioactive zinc stearate (containing ^{65}Zn) was prepared and then the γ radiation intensity from the rubber samples was measured to determine the zinc stearate dispersion. The studies reported in this work are:

1. Analysis of simple eutectic alloys of components of the sulfur-based vulcanization system.
2. Application of the ^{65}Zn radioisotope in dispersion tests of zinc stearate. How this method was used to determine sulfur and zinc oxide dispersion is described elsewhere.[6–10]
3. Determination of the dispersion level of

Table I The Composition of Alloy Mixtures

No.	Mixture Composition
1	oiled soluble sulfur + stearic acid
2	oiled soluble sulfur + zinc stearate
3	oiled soluble sulfur + ZnO
4	stearic acid + ZnO
5	zinc stearic + ZnO
6	oiled soluble sulfur + stearic acid + ZnO
7	oiled soluble sulfur + zinc stearate + ZnO

mineral oils in oiled soluble and Crystex insoluble sulfur by an ultraweak chemiluminescence (CL) measured by means of a high-sensitivity slow-can charge-coupled device (CCD camera).

EXPERIMENTAL

Materials

The following materials were used in the investigations described here:

- Polymeric granulated sulfur Crystex OT33 containing 30–35% processing oil, made by Kali-Chemie AKZO (Germany; received in 1997) and mineral sulfur containing 5% processing oil;
- Chemically pure n-Hexane, Riedel No. 15671 (saturated with α-sulfur);
- Commercial-grade stearic acid (Stearin IIIA, Setuza s.a., Czech Republic), used in the production of the rubber compounds;
- Commercial-grade zinc oxide (Bedzin Metallurgical Plant, Poland), used in the production of the rubber compounds;
- Zinc stearate (CECA s.a., Immeuble Iris, 92062 Paris, La Defense, Cedex, France).

Testing Conditions

Creating the Eutectic Alloys

To obtain alloys, 12 g of the components (Table I) at different weight ratios was put into glass test tubes and heated in a sand bath up to 160°C. The decreasing temperature was measured by a PT-100 thermoresistor, the data obtained were processed using Metex computer software, and then phase diagrams were drawn. The mixture of oiled soluble sulfur, zinc stearate, and ZnO was se-

Table II Constants of Crosslinking Rate (k) and the Activation Energy of Crosslinking (E_s) of Natural Raw Rubber by Sulfur [11]

Vulcanizing System	$k \times 10^2$, min^{-2}	E_s, kcal/mole
S_8	0.6	35
$S_8 + \mathrm{ZnO}$	0.8	35
$S_8 + \mathrm{ZnO} + \mathrm{zinc\ stearate}$	9.2	19

lected for this experiment because such ingredients are commonly used in a sulfur-based vulcanizing system and have known parameters of the kinetics of curing (Table II).

Analysis of Zinc Stearate Dispersion

The technical preparation of zinc stearate contained 10.5–11.3 wt % zinc. It was activated in quartz capsules. The neutron flux was 1×10^{12} neutrons/cm^{2}s, and the activation time was 4 h. The radioactive material contained ^{65}Zn with a specific activity of 1 MBq calculated on 1 g of zinc. Next, the radioactive zinc stearate was mixed with the inactivated preparation at a ratio of 1:10 to obtain the homogeneous mixture. The variation coefficient of the ^{65}Zn dispersion in this mixture was 4.8%. The γ-radiation intensity of the samples was measured for 100 s on an automatic γ spectrometer of the Tesla type with a NaJ (Tl) crystal.[7] The measurements were performed in the calibrated canal of the energy 1.118 MeV (γ radiation of ^{65}Zn).
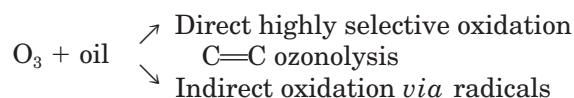
Using a laboratory scale, the tread-rubber compound containing 3 wt % of the radioactive zinc stearate was prepared. The compound was homogenized for 15 min on the mixing mill at 40°C. From the rubber compound plate we cut out samples in the form of a dish 12 mm in diameter and 10 mm thick. The dispersion of zinc in the samples was analyzed immediately after they were obtained and then after storage at 20, 40, and 60°C. Storage times were 24, 48, 144, 216, and 312 h. Each sample was sliced into 1-mm thick layers, and the intensity of radiation was measured for each weighed layer.

Determination of Degree of Dispersion of Mineral Oils in Soluble and Crystex Sulfur

The Molecular Light Imager LB 981 (called a CCD camera) made by EG&G Berthold (Germany) is designed for acquisition and processing of the images from luminescent samples when a highly sensitive measurement is needed (Fig. 1). A back-illuminated CCD sensor has the spectral sensitivity of 180–1100 nm and 40% quantum efficiency at 650 nm and 512×512 pixels. It operates at a temperature of 200 K and achieves thermal noise of electrons per second as low as 1 e$^-$/1000 s and a readout noise of 6 e$^-$. Powerful WinLight software operating on a Windows operating system controls all parameters of the camera. Quantitative analysis of the surface intensity of CL (CL flux in counts/pixels) was performed using a standardized procedure versus the radioluminescent ^{63}Ni–porcelain incorporated standard.

In the present study of both oiled soluble sulfur and insoluble Crystex OT-33 sulfur, we have used a CCD camera to monitor the surface intensity (I) and kinetics [$I = f(t)$] of an ultraweak chemiluminescence of mineral oils contained in sulfur granules. Before testing these samples were subjected to oxidative deterioration stimulated by ozonization.[12] The reaction of O_3 with organic oils (C=C content) can proceed directly or indirectly as follows:

$$O_3 + \mathrm{oil} \quad \nearrow \begin{array}{l} \text{Direct highly selective oxidation} \\ \quad \text{C=C ozonolysis} \end{array}$$
$$\searrow \text{Indirect oxidation } via \text{ radicals}$$

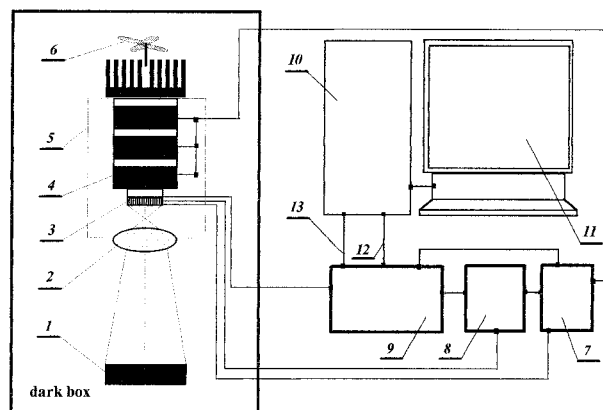The deactivation of excited states of radicals and products results in CL. We can measure the CL

Figure 1 Structure of the Molecular Light Imager LB 981 (CCD camera): 1—sample; 2—lens; 3—CCD senor; 4—thermoelectric cooler at −73°C; 5—camera; 6—ventilator; 7—power supply, 8—thermostatic chamber; 9—camera control and interfaces; 10—computer and software; 11—color screen; 12—data of camera control transmission; 13—image signals transmission.

Table III   The Schema of CCD Camera Experiments

No.	The Marking of Samples
1	radioluminescence standard
2	background of standard
3	background of apparatus
4	oiled soluble sulfur - nonozonized
5	oiled soluble sulfur - ozonized
6	oiled soluble sulfur extracted with 30 ml hexane, ozonized
7	oiled soluble sulfur extracted with 2×30 mL hexane, ozonized
8	oiled soluble sulfur extracted with 3×30 mL hexane, ozonized
9	oiled soluble sulfur extracted with 4×30 mL hexane, ozonized
10	Crystex OT 33 - nonozonized
11	Crystex OT 33 - ozonized
12	Crystex OT 33 - extracted with 30 ml hexane, ozonized
13	Crystex OT 33 - extracted with 2×30 mL hexane, ozonized
14	Crystex OT 33 - extracted with 3×30 mL hexane, ozonized
15	Crystex OT 33 - extracted with 4×30 mL hexane, ozonized

intensity, I, and infer from that the number of $C{=}C$ bonds because the number of emitted photons depends on the number of $C{=}C$ bonds on the surface area of ozonized samples. In the first experiment ozonized elemental sulfur and oiled soluble sulfur used in rubber technology were (1) prepared, and then (2) calibrating curves were drawn as follows:

(1) 1.5 g of elemental (or oiled soluble) sulfur in porcelain cuvette was ozonized using a glow discharge ozone generator at an O_2 flow rate of 0.5 m^3/h and a temperature of 20°C for 70 min. The ozone concentration was 30%. The intensity of the chemiluminescence was recorded after each hour of exposure time in the dark box of the CCD camera (Fig. 1).
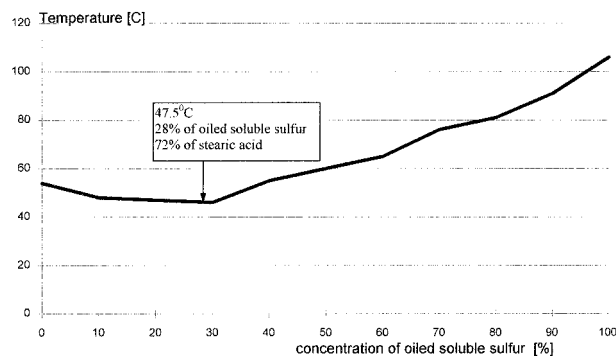

Figure 2   Phases' diagram for the mixture of oiled soluble sulfur and stearic acid.

(2) 6 g of oiled sulfur was weighed in a 2A3-type filter crucible and assembled into a suction filter flask, drenched with 30 mL of n-hexane, and stirred briefly; then the operation was repeated three times for soluble sulfur and 12 times for Crystex OT33 sulfur (n-hexane was saturated with α-sulfur). Finally, the n-hexane was removed by suction; the crucible dried for 45 min at 70°C in the drying oven, and after cooling in the desiccator, the crucible was reweighed. The oil content in soluble and Crystex sulfur was calculated. Then 1, 2, 3, 4, and 5 mL of condensed hexane solution was added into 1 g of pure sulfur from the crucible to produce different concentrations of oil. Here 1 mL of n-hexane solution contained 0.00685 g of oil for soluble sulfur and 0.09715 g for Crystex OT 33. After saturation, samples were dried, ozonized, and inserted in the dark box of CCD camera. Then, the intensity of CL was recorded after each hour of exposure time.

In the next experiments the extracted samples of different sulfurs were tested (Table III).

For testing, 2 g of sulfur samples were weighed in the 2A3 filter crucible and assembled into a suction filter flask, eluted with a 30-mL batch of n-hexane, dried for 45 min at 70°C in the drying oven, and cooled in the desiccator. Next, ozonized samples were inserted in the dark box of CCD
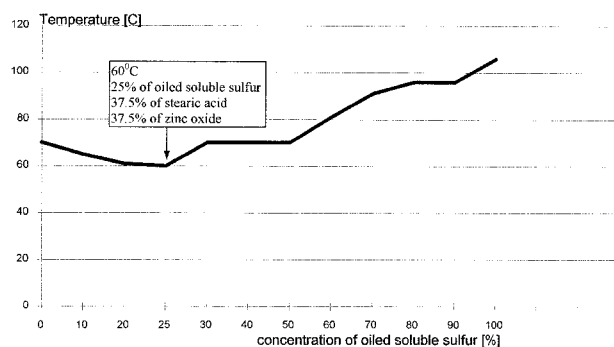
Figure 3 Phases' diagram for the mixture of oiled soluble sulfur–stearic acid–zinc oxide for the ratio 1:1 stearic acid:zinc oxide.

camera, and the CL intensity was recorded after each hour of exposure time.

RESULTS AND DISCUSSION

1. The analysis of phase diagrams of tested mixtures shows that oiled soluble sulfur and stearic acid at the weight ratio of 28:72 forms the eutectic alloy. The melting point of the eutectic was 47.5°C (Fig. 2). The tested soluble sulfur contained 2.26 wt % of oil. Figure 3 shows the phase diagram of the alloy of the oiled soluble sulfur–stearic acid–zinc oxide mixture. It is probable that the oiled sulfur (25%), stearic acid (37.5%), and zinc oxide (37.5%) create the eutectic alloy, with a melting point of 60°C.

The phase-diagram analysis of the oiled soluble sulfur, zinc stearate, and zinc oxide (Fig. 4) confirms the formation of the eutectic alloy at 28% oiled sulfur and 36% of both zinc stearate and zinc oxide. Its melting point increased to 79°C. The oil, contained in the sulfur, behaved specifically. It was brown and collected at the bottom of the glass tube. The oil dispersion in soluble sulfur also essentially influenced the shape of the cooling sulfur curves. Samples that were collected from different areas of the oiled soluble sulfur for testing showed variations of the melting point from 90 to 112°C. At 88–96°C on cooling curves we observed the temperature growth that resulted from the transition of α-rhombic sulfur into β-monoclinic sulfur as the isothermal change of the thermal capacity, enthalpy, and entropy. In particular, the systems with zinc oxide play an important part in determining the formation of simple eutectic alloys. The adsorption of stearic acid and sulfur in the form of eutectic alloys on zinc oxide causes the

additional increase in the dispersion of particles of these components as a consequence of the retarding of the adsorbed components' crystallization and the formation of a large number of nuclei. Simultaneously, we observed that the addition of zinc oxide to alloys heightens the melting point of the eutectic (Figs. 3 and 4). This fact may change the conformation of the analyzed component molecules at a suitable ratio in the eutectic alloys. Crystal defects and the increase in dispersion exhibit higher chemical reactivity. We should remember that the use of nonuniformly oiled soluble sulfur influences its behavior in the preparation of eutectic alloys. These facts must be considered if the degree of dispersion and the behavior of components of sulfur-based vulcanizing systems are to be accurately determined. The influence of the degree of mixing of the components on the testing results was ascertained in all eutectic experiments.

2. The statistical characteristics of zinc stearate dispersion were calculated for 1 g of its layer. In all results the decay correction of the radioisotope ^{65}Zn was considered.

Until 216 h of storage time, rubber compounds at $20-60°C$ improve dispersion of zinc stearate (Tables IV–VI). Unfortunately, too long a storage time aggravates this dispersion in all samples. It was found that zinc stearate doesn't bloom from the rubber compound at a 3% concentration, and, therefore, no problems related to changes in its concentration within these rubber compounds could be expected during processing. This conclusion was made from analyzing radiation measurements of rubber adjacent layers during storage under different conditions.

3. All tested oiled sulfur samples exposed to O_3 exhibit ultraweak CL lasting more than 4 h.
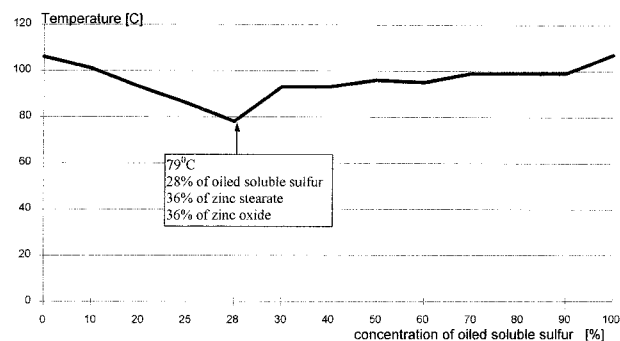

Figure 4 Phases' diagram for the mixture of oiled soluble sulfur–zinc stearate–zinc oxide for the ratio 1:1 zinc stearate:zinc oxide.

Table IV   Statistical Parameters of Radiation Intensity Results in Rubber Compound Stored at 20°C

	Storage Time, h					
	0	24	48	144	216	312
Number of samples	50	20	16	20	20	20
Average radiation intensity $c/100s \cdot g$	542	552	527	503	471	485
Standard deviation $c/100s \cdot g$	68	63	51	49	29	49
Skewness	0.87	−0.31	0.55	−0.59	−0.24	0.51
Kurtosis	4.26	3.89	2.57	2.92	2.36	3.24
Confidence interval $c/100s \cdot g$	514–570	507–597	485–570	468–538	450–491	450–521
Variation coefficient %	12.5	11.4	9.7	9,7	6.2	10.1

The control of oiled soluble sulfur (not exposed to O_3) and elemental sulfur (exposed to O_3) does not exhibit ultraweak CL. This provides evidence that pure sulfur does not emit any CL during the tests. The images of ultraweak CL and the kinetics $[I = f(t)]$ of these samples are shown in Figures 5 and 6. Ozonized oil extracted from two samples of oiled sulfur behave differently. They always produce a higher intensity of CL than samples of sulfur after extraction, which means that ozonized oil in soluble sulfur exhibits chemiluminescence and may be analyzed quantitatively.

In the next experiment we used the CCD camera to prepare the calibrative curves (chemiluminescence as a function of known concentration of oil) for oiled soluble sulfur (Fig. 7) and polymeric

Table V   Statistical Parameters of Radiation Intensity Results in Rubber Compound Stored at 40°C

	Storage Time, h					
	0	24	48	144	216	312
Number of samples	50	20	20	20	20	20
Average radiation intensity $c/100s \cdot g$	542	529	527	512	504	501
Standard deviation $c/100s \cdot g$	68	37	20	47	62	41
Skewness	0.87	−0.17	−1.08	1.91	−0.32	0.08
Kurtosis	4.26	3.19	3.53	3.99	3.32	3.25
Confidence interval $c/100s \cdot g$	514–570	503–556	512–541	478–546	460–549	471–531
Variation coefficient %	12.5	7.0	3.8	9,2	12.3	8.2

Table VI Statistical Parameters of Radiation Intensity Results in Rubber Compound Stored at 60°C

	Storage Time, h					
	0	24	48	144	216	312
Number of samples	50	20	16	20	20	20
Average radiation intensity c/100s · g	542	508	547	523	529	515
Standard deviation c/100s · g	68	38	41	25	60	55
Skewness	0.87	0.30	−0.26	1.23	0.22	0.37
Kurtosis	4.26	4.21	3.82	3.07	4.56	3.78
Confidence interval c/100s · g	514–570	480–535	513–581	505–541	486–572	475–555
Variation coefficient %	12.5	9.5	7.5	4,8	11.3	10.7

Crystex OT sulfur (Fig. 8). Also the kinetics of the decay of an ultraweak chemiluminescence (Figs. 9 and 10) were determined. The calibrative curves show that the number of emitted photons depends on the amount of oil (accepted as directly proportional to the concentration of C=C bonds) on the surface of ozonized samples. This method can be used for quantitative determination of oil content in different samples of sulfur. The control oils gave measurable CL signals at $100-240 \times 10^3$
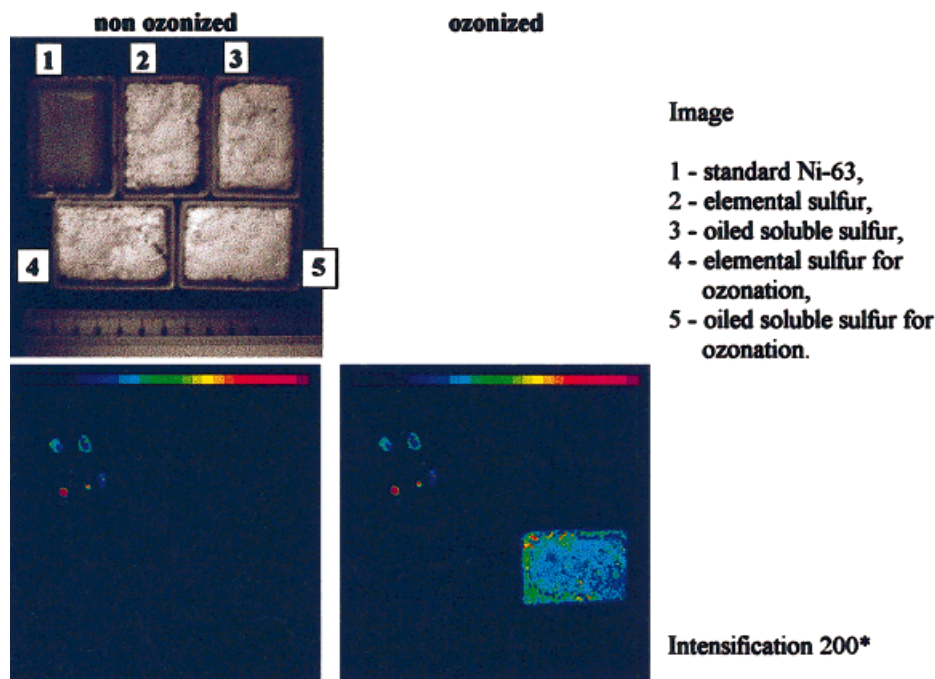
Figure 5 Images of an ultraweak chemiluminescence from elemental sulfur and oiled soluble sulfur. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
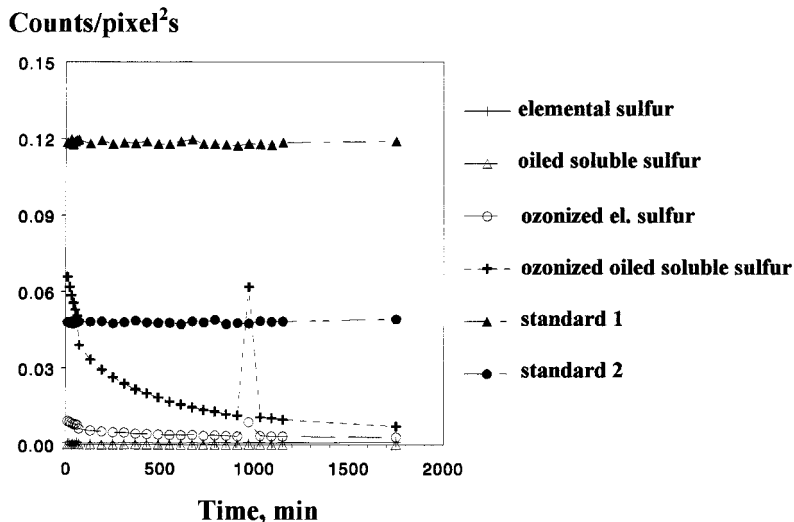
Counts/pixel^{2}s

Figure 6 Kinetics of the decay of an ultraweak chemiluminescence of elemental sulfur and oiled soluble sulfur.

photons/cm^{2}s for soluble sulfur (Fig. 9) and 100–1000 × 103 photons/cm^{2}s for Crystex OT sulfur (Fig. 10). These typical kinetic curves $[I = f(t)]$ clearly show the fast decay of a chemiluminescence and a possibility of quickly obtaining the results of the analyses.

Figures 11 and 12 show changes in oil dispersion on the ozonized sulfur surface. Samples were prepared on a laboratory scale and at different oil concentrations. To estimate oil dispersion, in a porcelain cuvette the surface of each sample was

divided into eight parts (Figs. 13 and 14, 4 partial samples) At the precise point where oil was carried onto a sulfur surface, satisfactory dispersion was not obtained, particularly in Crystex sulfur. Chemiluminescence from this oiled sulfur is incomparably more intense than that from unoiled samples, which may mean that oil distribution is not homogenous within sulfur granules during the manufacturing process and probably could also be preserved in rubber compounds.
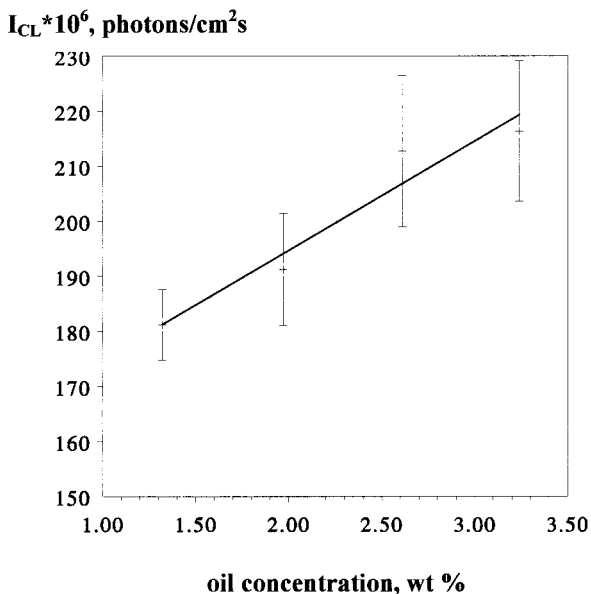
$I_{CL}*10^6$, photons/cm^{2}s

Figure 7 Calibrative curve for oiled soluble sulfur.
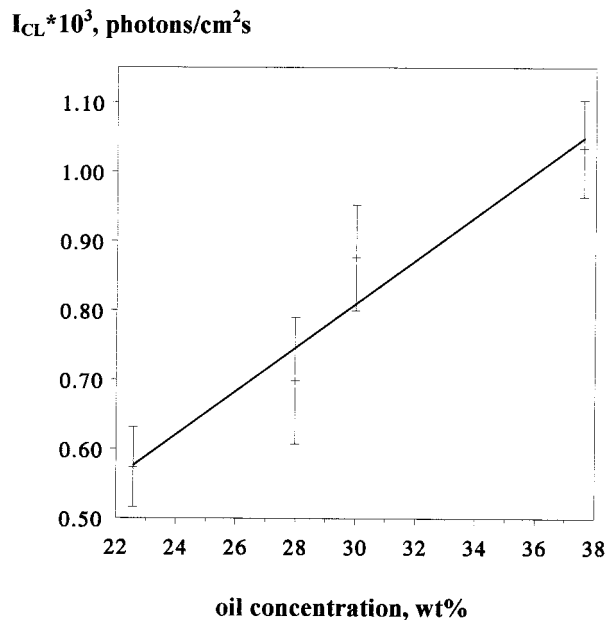
$I_{CL}*10^3$, photons/cm^{2}s

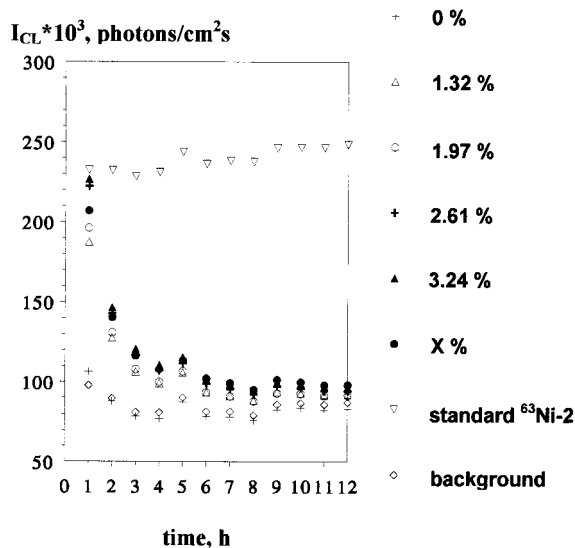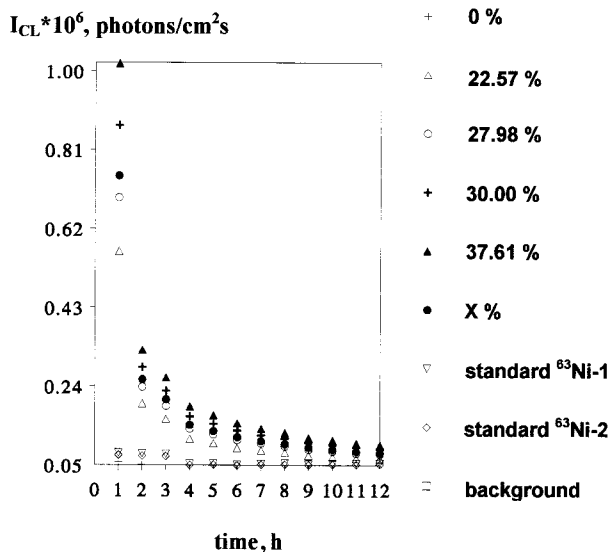**Figure 8** Calibrative curve for Crystex OT sulfur.

Figure 9 Kinetics of the decay of an ultraweak chemiluminescence of oiled soluble sulfur (total samples) X%—unknown concentration of oil.

The sequence of samples taken for testing, images of chemiluminescence from ozonized oiled soluble sulfur and from Crystex sulfur, and tested surface areas are shown in Figures 13 and 14. Successive images and the kinetics $[I = f(t)]$ for ozonized oiled sulfurs of both the soluble and Crystex types after n-hexane elution (Figs. 15 and 16) show that the second portion of n-hexane completely rinses the oil from the soluble sulfur. The
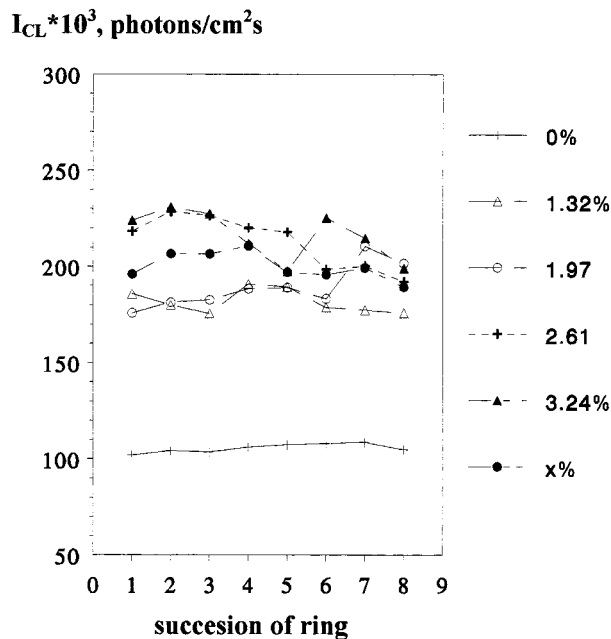

Figure 11 Oil dispersion in soluble sulfur samples (partial samples) X%—unknown concentration of oil.

elution of oil was performed according to a commonly used method.[14] It was found that 4×30 mL of n-hexane doesn't sufficiently rinse the oil from Crystex sulfur. In this case, the following results of oil concentration averaged from 30 samples eluted with solvent were obtained:
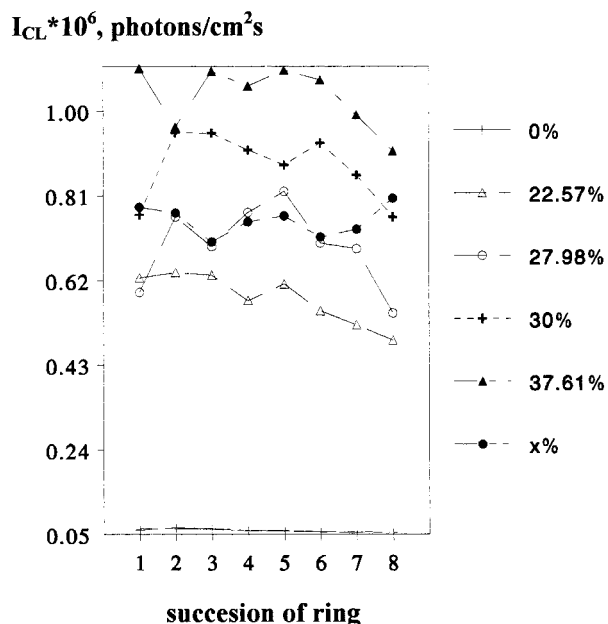

Figure 10 Kinetics of the decay of an ultraweak chemiluminescence of oiled Crystex OT sulfur (total samples) X%—unknown concentration of oil.

Figure 12 Oil dispersion in Crystex OT sulfur (partial samples) X%—unknown concentration of oil.
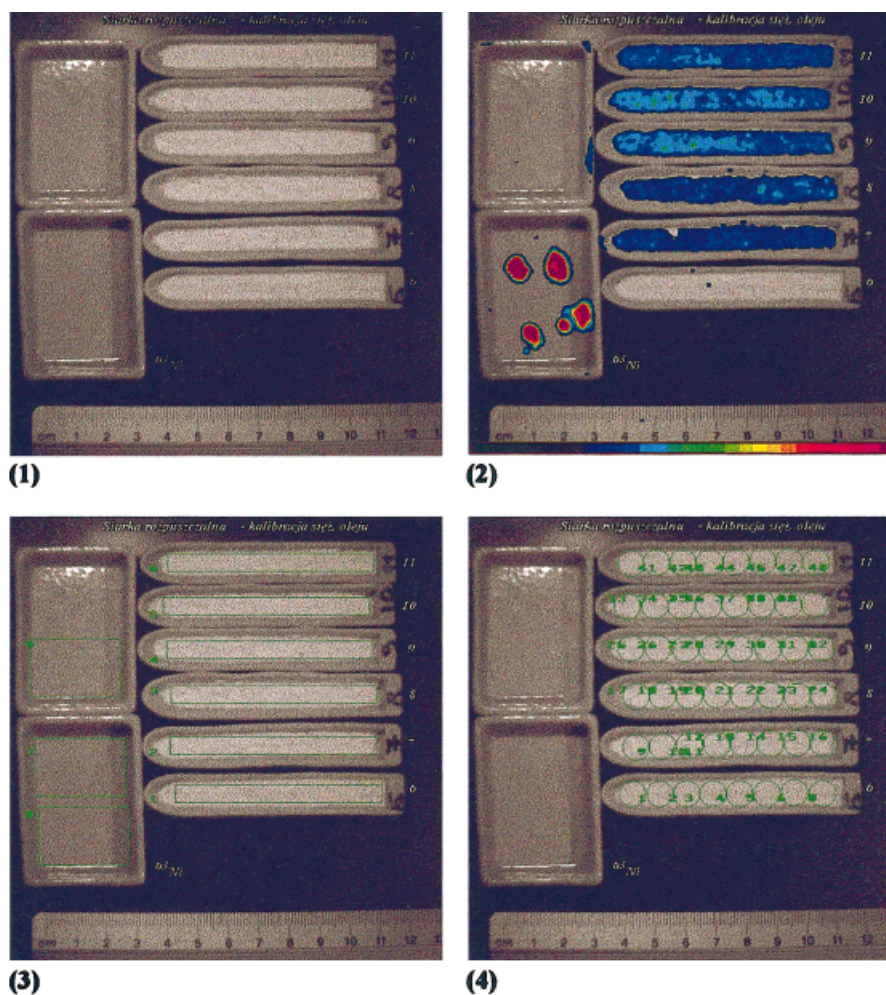
Figure 13 Images of a chemiluminescence from ozonized oiled soluble sulfur at different concentrations of oil: (1) sequence of samples; (2) images of a chemiluminescence after Pseudo Color[13]; (3) determined areas of a chemiluminescence—total samples; (4) determined areas of a chemiluminescence—partial samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

In the first experiment 4 30-mL portions of n-hexane produced 31.5% oil in sulfur. In the second experiment 8 30-mL portions of n-hexane produced 31.9% oil in sulfur. In the third experiment 12 30-mL portions of n-hexane produced 32.4% oil in sulfur. These tests demonstrate that 12×30 mL of n-hexane deprive Crystex of oil.

It was also observed that determining the oil content in polymeric sulfur by a commonly used weight method is not sufficiently precise for this purpose. We believe the CCD camera gives a much more accurate evaluation of the oil content in sulfur. By using both these methods, it was found that the distribution of oil in the production samples of polymeric sulfur is not uniform. Because of this, the results of oil content evaluation depend on the location of the sample collecting.

CONCLUSIONS

Analysis of phase diagrams of molten mixtures shows that all oiled soluble sulfur + stearic acid, oiled soluble sulfur + stearic acid + zinc oxide, and oiled soluble sulfur + zinc stearate + zinc oxide form eutectic alloys at a suitable ratio of the components. The additions of zinc oxide and zinc stearate heighten the melting point of the eutectic alloy. In our earlier work[8] it was demonstrated that at storage temperatures higher than 42°C,
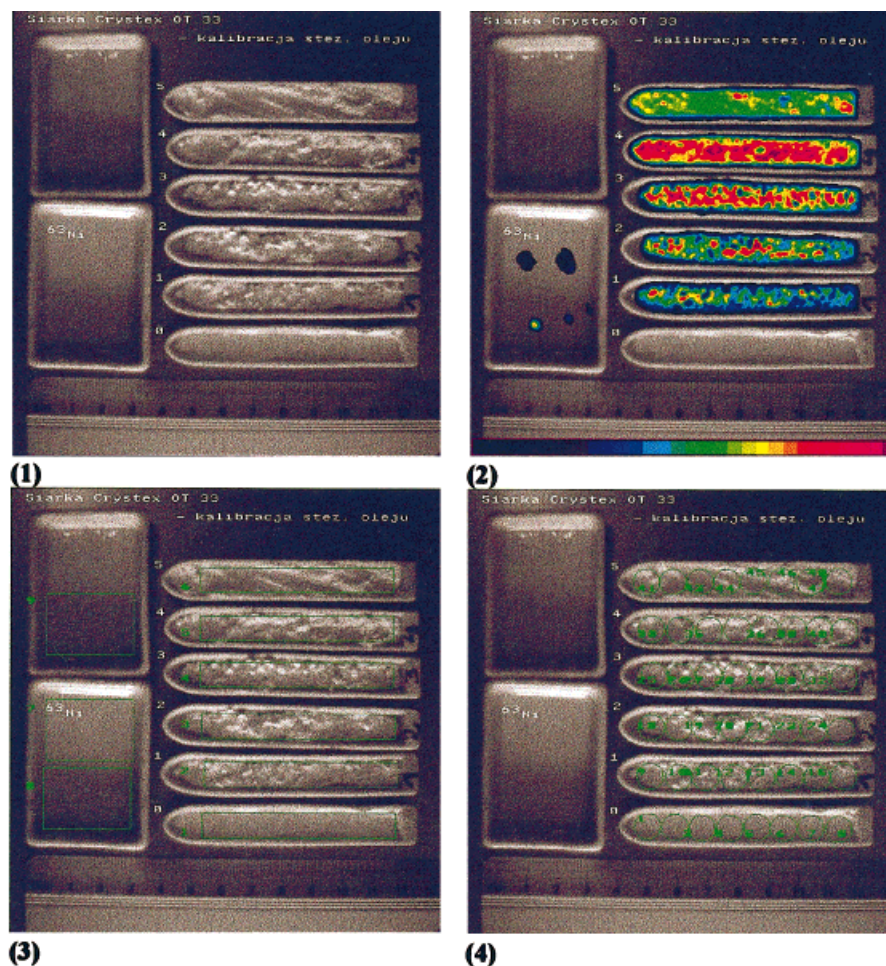
Figure 14 Images of a chemiluminescence from ozonized oiled Crystex OT sulfur at different concentrations of oil: (1) sequence of samples; (2) images of a chemiluminescence after Pseudo Color; (3) determined areas of a chemiluminescence—total samples; (4) determined areas of a chemiluminescence—partial samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

the process occurring in rubber compounds is the reverse of sulfur blooming. We believe that storage at least at the eutectic temperature can protect a rubber compound from blooming sulfur as a component of eutectic alloys on the rubber surface because they have a melting point far below that of soluble sulfur. Therefore, the distribution of analyzed ingredients within the rubber compound must be controlled to help in obtaining eutectic alloys during rubber processing.

The determination of zinc stearate dispersion in rubber compounds by a radioisotopic method suggests that this ingredient does not bloom from the compounds at 3% concentration, but its dispersion was more than for the polymeric one. This difference in oil distribution uniformity should influence the final dispersion of sulfur within rub-

ber compounds and the conditions for the creation of eutectic alloys. CL imaging may offer a fast and sensitive method for the determination of oil dispersion in both soluble and polymeric sulfur. The application of radioisotopes for this purpose could be more difficult. The described methods characterize the comparable sensitivities. The ultrasensitive slow-scan CCD camera is suitable for measurements and imaging of extremely weak CL accompanying oxidative deterioration of oils, where only a minimum of light is available. Parameters of the micro system of the CCD camera allow it to take simultaneous images from a great number of samples, using, for example, micro plates. The increase in CL intensity correlates with the rate of oxidative deterioration of oils exposed to ozone and their concentrations.
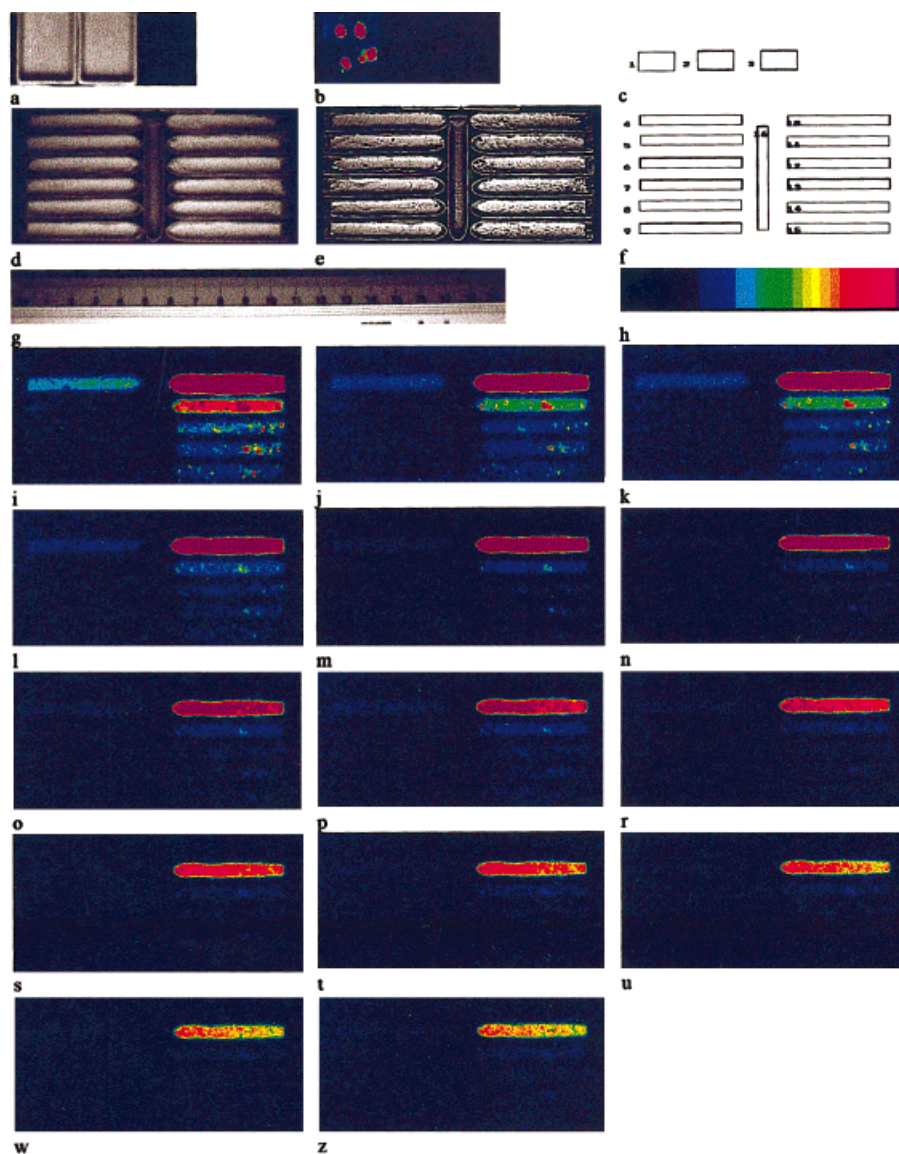
Figure 15 Successive images of a ultraweak chemiluminescence from ozonized oiled soluble sulfur (f,4—9) and Crystex OT 33 sulfur (f, 10—15) after *n*-hexane elution. Images: (a) radioluminescence standard, (b) a radioluminescence standard after Pseudo Color; (c) measurement ranges (1—standard, 2—background of standard, 3—background of apparatus); (d) arrangement of sulfur samples; (e) irregularity of sulfur surface; (f) numeration of sulfur samples (4—oiled soluble sulfur; nonionized; 5— oiled soluble sulfur, ionized; 6—oiled soluble sulfur-extracted 4 × 30 mL hexane, ozonized; 7—oiled soluble sulfur extracted 2 × 30 mL hexane, ozonized; 8—oiled soluble sulfur extracted 3 × 30 mL hexane, ozonized; 9—oiled soluble sulfur extracted 4 × 30 mL hexane, ozonized; 10—Crystex OT 33, nonozonized; 11—Crystex OT 33, ozonized; 12—Crystex OT 33–extracted 30 mL hexane, ozonized; 13—Crystex OT 33–extracted 2 × 30 mL hexane, ozonized; 14—Crystex OT 33–extracted 3 × 30 mL hexane, ozonized; 15—Crystex OT 33–extracted 4 × 30 mL hexane, ozonized); (g) line scale; (h) Pseudo Color scale; (i)–(z) successive images. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]
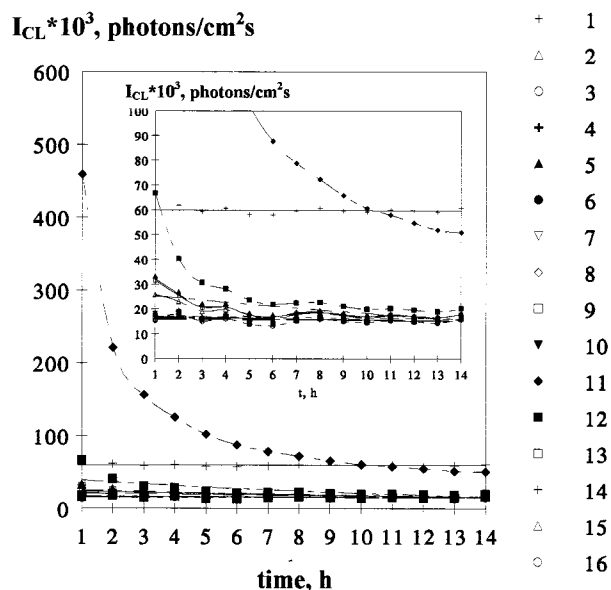
Figure 16 Kinetics of the decay of an ultraweak chemiluminescence of ozonized oiled soluble sulfur and Crystex OT 33 after *n*-hexane eluation: (1) intensity of chemiluminescence from standard; (2) background of standard; (3) background of apparatus; (4)–(9) elauted soluble sulfur; (10)–(15) eluated Crystex OT 33; (16) background of porcelains.

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