

# Chemiluminescence – mystery of cold light

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## Introduction

Luminescence phenomena, such as the aurora borealis, phosphorescence of the sea, luminescence of living organisms, phosphorescent wood or phosphor have fascinated man since ancient times. Aristotle was the first one who described “cold light” in dead fish, fungi and the luminous fireflies [1].

The term of luminescence was introduced in 1888 by E. Wiedemann. He stated that certain compounds are capable of emitting light without previous heating. Wawilow generalized this definition and stated that luminescence is the excess of the molecule light radiation over thermal radiation of the same molecule in the given spectral region and temperature. Luminescence is characterized by limited duration (do not stop immediately after excitation decay) [2].

Chemiluminescence is observed among aromatic and heterocyclic compounds including dyes (fluorescein, eozyn), biological compounds (chlorofil, carotenoid, certain vitamins and hormones) [3].

The current classification of luminescence phenomena is based on the categorization proposed by Wiedemann and depends on excitation mechanisms of molecule [4]. Luminescence phenomena are classified as follows:

- **Photoluminescence** – emission produced by the absorption of ultraviolet, visible or infrared radiation. Based on duration between absorption and emission of photons, fluorescence and phosphorescence are distinguished. The fluorescence occurs when time between absorption and emission of light is no longer than  $10^{-8}$  s. If the time between absorption and emission of light is longer than  $10^{-8}$  s the phosphorescence occurs
- **Thermoluminescence** – emission from solids induced by heating
- **Candoluminescence** – emission from incandescent solids
- **Triboluminescence** – emission induced by shaking, rubbing or crushing substance
- **Crystalloluminescence** – emission from crystallization
- **Electroluminescence** – emission from electrical discharges
- **Sonoluminescence** – emission from exposure to ultrasonic waves in solution
- **Bioluminescence** – emission from living organisms or biological systems (glowworm, bacteria, fungi, crustaceans)
- **Oxyluminescence** – emission from polymers induced by oxidation
- **Electrogenerated chemiluminescence** – emission produced at an electrode surface
- **Chemiluminescence** – emission of the ultraviolet, visible or near infrared radiation by molecules or atoms resulting from chemical reactions. Chemiluminescence takes place at room temperature in gas, liquid and solid phase [3].

In 1877 Polish scientist Radziszewski reported the chemiluminescence which was exhibited by the synthetic organic compound lophine (2,4,5-triphenylimidazole). He found that lophine emitted green light upon reaction with oxygen in the presence of strong base [5].

In general, two types of chemiluminescence mechanisms are distinguished (Fig. 1).

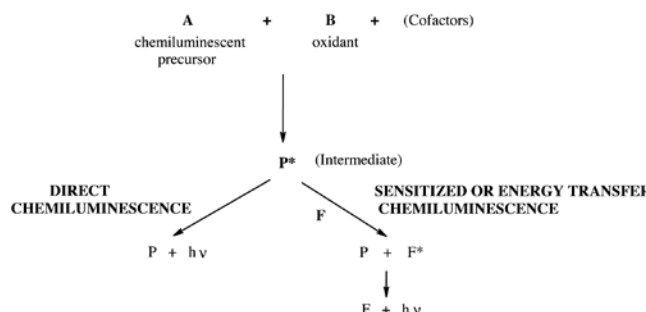


Fig. 1. Types of chemiluminescent reactions

In a direct reaction a substrate (A) and an oxidant (B) in the presence of cofactors react to form an intermediate product in an electronically excited state which relax to the ground state with photon emission.

An alternative for compounds producing ultraweak chemiluminescence is indirect sensitized chemiluminescence based on an effective energy transfer process from the excited species (P\*) to a fluorophore (F) that after excitation is released to its ground state with photon emission.

Therefore the substrate (A) is responsible for light emission or acts as the energy transfer donor. The catalysts, enzymes or metal ions, reduce the activation energy and update chemiluminescence efficiency. Cofactors convert the substrates into a form capable of reacting and interacting with the catalyst to provide efficient leaving groups.

The excitation is a decisive step in chemiluminescent processes. Spontaneous light emission during reaction requires the presence of the following conditions. First, the reaction must be highly exothermic (40–70 kcal/mol) in order that the chemiluminescence occurred in the visible region (400–750 nm). This condition is related with redox reactions in the presence of oxygen and hydrogen peroxide or similar oxidants. Some of the energy produced must be channeled into a reaction pathway in which at least one of the upper vibrational levels of the reactants (probably corresponding to the transition state of the initial reaction) has the same energy and a comparable geometrical structure as an upper vibrational level of the lowest excited singlet state of a emissive product of the reaction. Second, chemiluminescence will occur when  $\Delta H_a^* \leq \Delta H_a$ , in which  $\Delta H_a$  is the enthalpy of activation for “dark” reaction competing with the chemiluminescent pathway, whose enthalpy of activation is  $\Delta H_a^*$ . Additionally, the lowest excited singlet state of the fluorophore has the same geometrical configuration as the ground electronic state of the reactant.

Chemiluminescence quantum yield is the parameter which determines the intensity of emission of light. In order the efficiency of the chemical energy transfer into chemiluminescence reaction ( $\varphi$ ) was significant, the equation 1 must be preserved:

$$\varphi = \varphi_C \times \varphi_E \times \varphi_F \quad (1)$$

where:

$\varphi_C$  – the chemical yield of excited product formation

$\varphi_E$  – the excitation yield

$\varphi_F$  – the quantum yield of fluorescence of the light-emitting species

The quantum yield of chemiluminescence depends on the efficiency of the particular intermediate processes leading to the emission of light. Chemiluminescence emission is influenced by factors such as: the chemical structure of the chemiluminescent precursor, the nature and concentration of other substrates affecting the process and favoring other irradiative competition processes, the selected catalyst, the presence of metal ions, especially transition metals involved in the processing of the oxidant, the presence of energy transfer acceptors, temperature, pH, ionic strength and the type of the solvent. Molecules that are involved in chemiluminescence reactions (luminogenic compounds) are generally reduced species, such as molecules containing amino and hydroxyl groups and polycyclic aromatic ring systems [3].

### Liquid-phase chemiluminescence reactions

There are known numerous chemical reactions in which emission of light occurs. The most known are oxidation reactions by oxygen or hydrogen peroxide usually in the presence of catalyst – enzyme. The representative example is oxidation of luminol (5-amino-2,3-dihydro-1,4-phthalazinedione) in basic solution and in the presence of catalyst (Fig. 2).

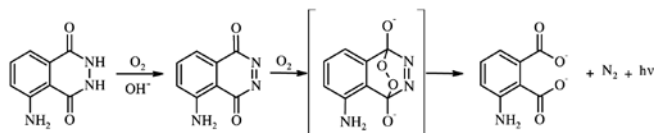


Fig. 2. Oxidation of luminol in the presence of hydrogen peroxide and catalyst

The oxidation of luminol often occurs in the presence of hydrogen peroxide and catalysts such as  $(\text{Fe}(\text{CN})_6)^{3-}$ ,  $\text{Cu}(\text{II})$  or  $\text{Co}(\text{II})$  in basic solution. A dianion of luminol is formed as a key intermediate. It reacts with oxygen or an alternative oxidizing agent to yield an excited state of the aminophthalate ion that is responsible for the emission of blue light in water and yellow-green in DMSO [6, 7]. The oxidation of luminol in basic solution is one of the best known and most efficient chemiluminescent reaction. A quantum yield of chemiluminescence in water and DMSO is of about 1–1.5% and up to 5%, respectively [8, 9]. The luminol reaction is used in direct assays for the determination of different oxidizing agents such as  $\text{H}_2\text{O}_2$ ,  $\text{O}_2$ ,  $\text{I}_2$  and in indirect assays for determination of glucose in the presence of enzymes such as peroxidase; metal ions and their complexes ( $\text{Cu}(\text{II})$ ,  $\text{Co}(\text{II})$ ,  $\text{Fe}(\text{III})$  etc.) and inhibitors ( $\text{Ag}(\text{I})$ ,  $\text{Ce}(\text{IV})$ ,  $\text{Ti}(\text{IV})$  etc.) [3].

Direct chemiluminescence is observed among limited group of organic compounds. These include indoles I [10], polydimethylaminoethylenes II [11] and Schiff's bases III [12] (Fig. 3).

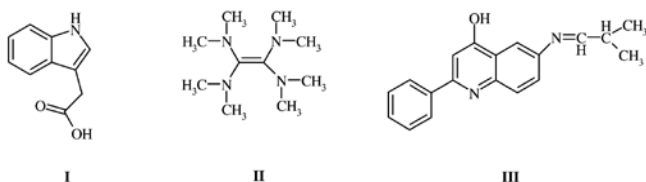
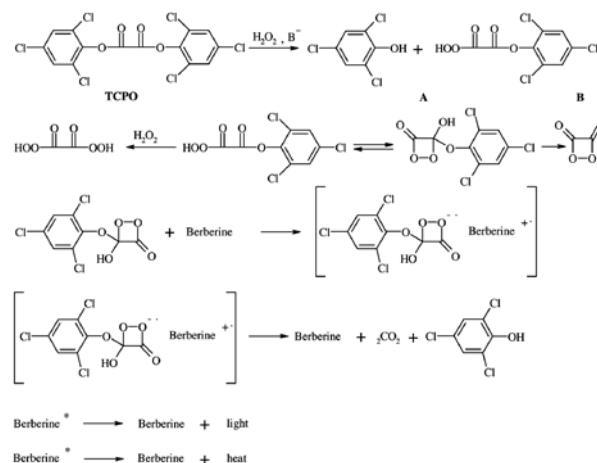


Fig. 3. Structure of direct chemiluminescent compounds

Another group of the most efficient chemiluminescence systems are peroxyoxalate derivatives (PO-CL) first reported in 1963 by Chandross [13]. The oxidation of oxalic acid derivatives with hydrogen peroxide in the presence of a fluorophore (9,10-diphenylanthracene) gave bright, long-lasting emission of blue light. The most frequently used oxalate derivatives are *bis* (2,4-dinitrophenyl) oxalate (DNPO) and *bis* (2,4,6-trichlorophenyl) oxalate (TCPO). A typical PO-CL system consists of the oxalate derivatives, hydrogen peroxide as oxidant and catalyst. The

intermediate products obtained in chemiluminescence are capable of producing an excited state of fluorophore responsible for emission of light. The example of sensitized peroxyoxalate chemiluminescence in the presence of berberine is presented in Figure 4.



where: B- sodium salicylate

Fig. 4. Mechanism of sensitized peroxyoxalate chemiluminescence in the presence of berberine

In chemiluminescence reaction the high-energy cyclic intermediates (dioxetane species A, B) are suggested. Excited molecule of fluorophore (berberine) emits intense yellow light via the chemically initiated electron exchange luminescence (CIEEL) mechanism [14].

The oxidation of oxalate esters in the presence of diluted anhydrous hydrogen peroxide, catalyst – sodium salicylate and sensitizers has practical application in Cyalume Technologies products known as chemical light sticks. High quantum yield of sensitizers lightening reached several dozen percent have essential influence on commercial success of the chemical light sticks. These products find several practical applications in military, police, emergency services but also in floats for fisherman, sports, tourism and entertainment.

Cyalume products are environmentally friendly, safe, non-toxic, non-flammable, non-breakable, weather conditions resistant and completely waterproof. Chemical light sticks are disposable, stop lightening after a determined time. The elastic tube flashlight filled with hydrogen peroxide and a breakable capsule with oxalate esters and sensitizers is subsequent practical development introduced by American Cyanamid Company. Chemiluminescence reaction is observed after snapping inner capsule and shaking the tube when the reagents are mixed together. Time of shining such flashlight depends on the composition and exploitation and last from 5 minutes to 12 hours [15].

Another efficient chemiluminescence compounds are acridine esters derivatives. Intense blue-green chemiluminescence during the oxidation of lucigenin (10,10'-dimethyl-9,9'-bisacridinium dinitrate) with hydrogen peroxide or oxygen in the presence of catalysts such as  $\text{Co}(\text{II})$ ,  $\text{Fe}(\text{II})$ ,  $\text{Fe}(\text{III})$ ,  $\text{Cu}(\text{II})$ ,  $\text{Cr}(\text{III})$ , or  $\text{Ni}(\text{II})$ , in alkaline solution, was first observed by Glue and Petsch in 1935. Mechanism of chemiluminescence of acridinium dimethylphenyl esters are presented in Figure 5.

Light emission from acridinium dimethylphenyl esters is generated in two steps. First, an initial treatment with acid rapidly converts the non-chemiluminescent pseudobase (A) to the chemiluminescent acridinium ester (B). Reaction of the acridinium ester (B) with alkaline hydrogen peroxide in the presence of cationic surfactant (cetyltrimethylammonium chloride) generates rapid chemiluminescence (< 5s). Excited state acridone (F) is believed to be the light emitting species in the chemiluminescence of acridinium phenyl esters. It is formed from decomposition of a high energy dioxetanone intermediate (E) or in direct formation from the dioxetane (D). Decomposition of the dioxetane intermediate (D)

or (E) is postulated to occur by electron transfer from the acridine nitrogen to the peroxide bond by a chemically initiated electron exchange luminescence (CIEEL) mechanism [16].

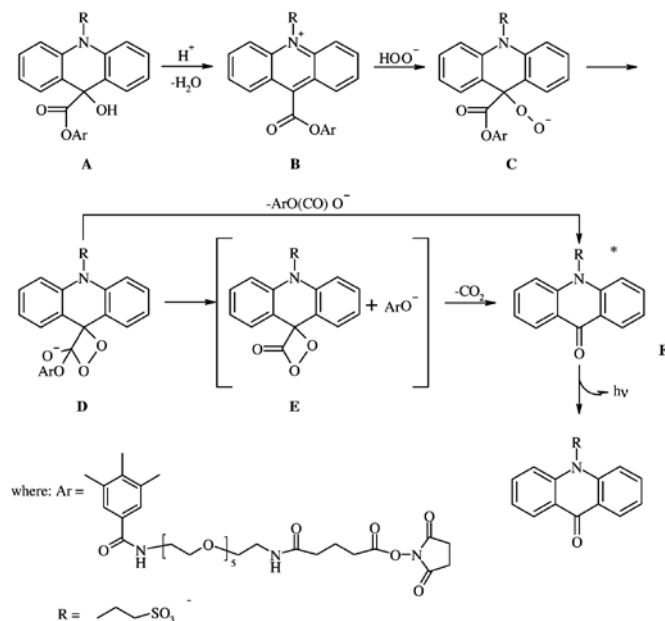


Fig. 5. Mechanism of chemiluminescence of acridinium dimethylphenyl esters

Chemiluminescence is widely applied in analytical chemistry due to some special advantages. It is characterized by high sensitivity ( $10^{-15}$  mol) and selectivity in comparison to other spectroscopic techniques. It is approximately  $10^5$  times more sensitive than absorption spectrophotometry and at least  $10^3$  times more sensitive than fluorimetry. Instrumentation used to measure chemiluminescence is relatively simple, because there is no necessity to use external light source compared to other measurement technique (photoluminescence processes). Then the problem related to scattering signals or instability of the external source is eliminated. Moreover, background photoluminescence signals are not observed as well. As opposed to photoluminescence processes this method do not cause nonlinearity or spectral interferences. In the case of low chemiluminescence quantum yield reactions it is possible to use more sophisticated instrumentation for the measurement of light intensity. Then, the use of special light detectors based on photon counting systems (PCS) or photomultiplier tube (PMT) systems, photodiodes or scintillation counters are required [17]. Because emission intensity is directly proportional to analyte concentration therefore chemiluminescence method enables to determine a wide variety of species that can participate in the process. Sensitized chemiluminescence allows to recognize of fluorophores and some substances which are not directly involved in the reaction but can generate products which are reactants in the chemiluminescence reaction. Molecule identification follows by determination of parameters such as excitation and emission spectra, decay times, polarization data. Chemiluminescence application opportunity with other techniques for example high-performance liquid chromatography (HPLC) [18, 19], capillary electrophoresis (CE) [20, 21] or flow injection analysis (FIA) [22, 23] provides qualitative and quantitative information of examined species in the gas, liquid and solid phases. Due to numerous advantages chemiluminescence is used as an analytical technique in many disciplines such as biomedical, pharmaceutical [24÷29], food analysis [30÷34], toxicological and environmental analysis [35÷41].

However, some limitations must be also considered. In combination with analytical technique such as HPLC or CE the lack of selectivity may occur. First, a significant chemiluminescence from solution may be caused by more than one analyte. Second, chemiluminescence

intensity depends on the variety of physic-chemical and environmental factors such as pH, temperature, ionic strength. As a result, separation conditions may not always match the optimum chemiluminescence. Moreover, because chemiluminescence intensity varies with duration of process therefore the emission spectra of investigated compounds can widely vary in particular chemiluminescence systems. In order to obtain the comparable results it is necessary to detect the signal in flowing stream at strictly defined periods [42].

### Gas-phase chemiluminescence

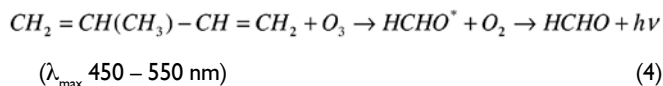
The application of chemiluminescence for determining components of a gas originates from the need to determine atmospheric pollutants. Owing to this method it is possible to detect pollution at the ppb (parts per billion) level. Because gas-phase radiative emission is competitive with irradiative processes, the quantum yield of the reaction and the emission spectrum vary with physical conditions such as gas composition, temperature and pressure. In order to obtain the emission in the UV/Vis range, highly exothermic reactions is required. That is possible in the case of atomic, radical recombination or redox reactions. Chemiluminescence enables to detect sulfur, nitrogen, phosphorus and ammonia compounds, olefins, hydrogen atoms in the presence of strong oxidants such as fluorine, chlorine dioxide and ozone. The most widely used reagent is ozone [43, 44, 46, 47]. In many cases, nitrogen/sulfur analytes may not react with ozone in the gas phase at room temperature, therefore pyrolysis process is necessary.

The chemiluminescence is exhibited by many compounds in the reactions with ozone. There are nitrogen oxide, sulfur oxide, unsaturated hydrocarbons such as alkenes, alkynes and aromatics [45].

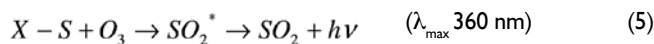
The best known and most frequently used is the reaction of nitrogen oxide with ozone is (equation 2, 3). As a result of the exothermic reaction (48 kcal/mol), the distinctive near-infrared broad centered around 1200 nm is emitted.



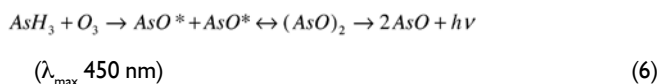
Among olefins, the attention is paid to isoprene (2-methyl-1,3-butadiene) that is very important industrial product used for synthetic rubber production that is a major biogenic compound. Isoprene is made by bacteria and vegetation during the process of photosynthesis. It is also the dominant hydrocarbon in human breath [48]. Isoprene chemiluminescence in the presence of ozone was demonstrated by Hills and Zimmerman in 1990 (equation 4) [49]. Excited state molecule of formaldehyde is responsible for emission of light in the wavelength region 450–550 nm. Chemiluminescence-based isoprene measurements are used for environmental air monitoring.



The chemiluminescence reaction in the presence of sulfur gases (equation 5) is actually more complicated in the real world. In comparison to  $NO + O_3$  system this reaction is much more exothermic (106 kcal/mol). The emission spectrum ranges from 280 to 460 nm and is centered around 360 nm. Excited molecule of  $SO_2$  has been found to be the principal emitter responsible for chemiluminescence. This fact was proved by chemiluminescence investigations of other sulfur compounds such as  $H_2S$ ,  $CH_3SH$ , DMS,  $(CH_3)_2S$ ,  $CS_2$ ,  $C_6H_5SH$  with ozone. If the sulfur/nitrogen containing analytes exist at low concentration, the separation methods are essential to apply [50÷53]. Gas-phase chemiluminescence is widely used for global atmospheric analysis [54, 55], emission from soils and vegetation [46, 47, 56] and in medicine [50, 57].



Arsenic is the most abundant element in the terrestrial crust [58]. Arsenic compounds can be found especially in groundwater used for drinking but also in seas, rivers, soils, air and in food resources [59, 60]. The hydride of arsenic ( $AsH_3$ ) is particularly toxic. Chemiluminescence of arsenic oxide in the presence of ozone for the first time was observed by Fujiwara et al. [61]. As a result of the reaction of  $AsH_3-O_3$  system a broad emission band is observed ranging from 350 to 600 nm centered at 450 nm (equation 6). Numerous detection techniques of arsenic hydride measurement in ozone-induced chemiluminescence were reported [62–64].



### Solid phase chemiluminescence

Some polymers exhibit weak chemiluminescence in the visible range when heated up in the presence of inert gas (air or oxygen). For the first time this phenomenon was observed by Ashby in 1961 from polypropylene [65]. Later, many important papers on chemiluminescence from polyolefins and polyamides [66–68], cellulose and biopolymers [69–73] were published. Emission of light during oxidation of polymers is called oxyluminescence [65] or oxychemiluminescence [74]. For chemiluminescence of polymers to be observed, oxygen must be present in the process [75–78].

Oxidation (autooxidation) is one of the most important processes responsible for degradation of polymers (Fig. 6) [79]. The first step (initiation) is the formation of primary radicals  $R^\cdot$  as a result of degradation of polymer materials by factors such as heat, light, catalysts (such as transition metals), radical initiators or impurities in the monomers. Radicals  $R^\cdot$  obtained rapidly react in the presence of oxygen to form peroxy radicals  $ROO^\cdot$ , which abstract hydrogen from the monomer and form an alkyl radicals  $R^\cdot$  and a hydroperoxides  $ROOH$ . Radicals generated from hydroperoxides  $ROOH$  decompositions again abstract hydrogen atoms. New macro radicals produce a variety of product species in an another autooxidation cycle process.

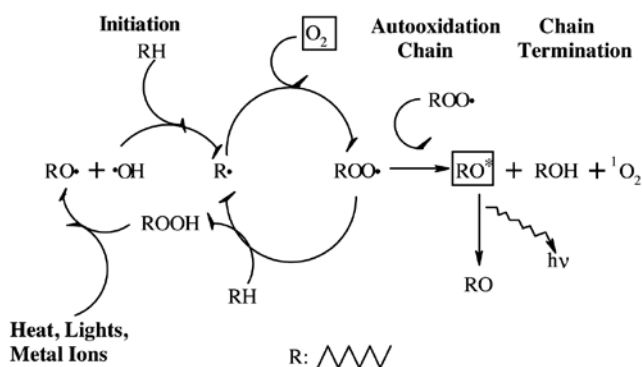


Fig. 6. The cycle of autooxidation

Termination of the propagation occurs in radical recombination reaction. When the oxygen pressure is suitably high, the termination occurs according to Russell mechanism (Fig. 7). As a result of bimolecular termination reaction of primary and secondary peroxy radicals an intermediate tetraoxide is obtained. Strongly exothermic (462 kcal/mol) the triplet ketone, singlet oxygen and alcohol are generated during its decomposition. Excited ketone emitting blue-violet (400–500 nm) light is the source of chemiluminescence emission from polymer [80, 81]. The termination mechanism was supported in other experiments concerning oxidation of hydrocarbon [82, 83].

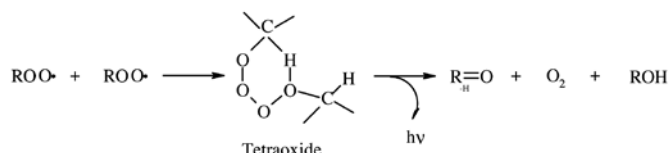


Fig. 7. Russell mechanism of chemiluminescence pathway

Peroxy radicals  $ROO^\cdot$  produced during decomposition of hydroperoxide are key intermediate in oxychemiluminescence [69, 84, 85]. Extensive research of chemiluminescence from polymers proved that various chemical and physical methods of excitation of polymer during heating are possible [86, 88]. Chemiluminescence can be induced by easily decomposable radical initiators introduced in polymeric materials [89, 90]. Recently, photo-induced chemiluminescence in the presence of xanthenes and triphenyl methane dyes have been reported [91]. Solid-phase chemiluminescence can be also used to evaluate the degree of degradation [92], to study the reaction mechanisms and oxidation kinetics [93, 94] or to assess the stabilization efficiency of additives such as antioxidants [95].

### Summary

Nowadays, it is general tendency in analytical chemistry to detect various species at extremely low concentration (in the range of femtomol). This trend is connected with environmental requirements that influenced the reduction of large amount of waste and pollutants generated in analytical processes. Chemiluminescence as an environmentally friendly method fulfills ecological prerequisite. It is of great importance because it provides high sensitivity and selectivity detection system.

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