

ROOM-TEMPERATURE LUMINESCENCE FROM KAOLIN INDUCED BY ORGANIC AMINES

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Abstract—Several new, room-temperature luminescent phenomena, resulting from the interaction of kaolin and various amino compounds, have been observed. The emission of light from kaolin pastes (treated with quinoline, pyridine, hydrazine, monoethanolamine, n-butylamine, and piperidine) was shown to decay monotonically over a period of hours to days. More light was released by a given amino compound after it was dried and purified. Hydrazine, in addition to the monotonically decaying photon release, produces delayed pulses of light with peak emission wavelength of 365 nm which last between several hours and several days. These photon bursts are acutely sensitive to the initial dryness of the hydrazine, both in the number of bursts and the integrated photon output. The amount of light and the capacity of the kaolin to produce the delayed burst appeared to be strongly dependent on preliminary heating and on gamma-irradiation, analogous to the dehydration-induced light pulse previously reported from the Ames Research Center. A small, delayed burst of photons occurred when piperidine and n-butylamine were removed by evaporation into an H₂SO₄ reservoir.

Key Words—Amine, Hydrazine, Kaolin, Luminescence.

INTRODUCTION

The release of photons from clay minerals which resulted from superficial dehydration produced by desiccation or by gentle heating, was reported by Coyne *et al.* (1981a, 1981b). The mechanism postulated for this photon release was mechanical stress on the crystal, produced during the drying process. The release of photons accompanying the removal of water by displacement by other solvents (rather than by evaporation), which is presumed to be a less "stressful" process, has been investigated. Organic amines have been shown to replace water of hydration on clay surfaces (Theng, 1974; van Olphen, 1977). In the present study, we found that photons were released when kaolin (or its chemical building blocks, silica and alumina) was mixed with organic amines of widely varying base strength.

EXPERIMENTAL PROCEDURES

Solid substrates: properties and characterization

Kaolin, Fisher lot 753828, was used without further purification. The surface area was measured by Pacific Sorption Service, Chico, California, to be 15 m²/g by B.E.T. The hygroscopic water content was 3–4%. The cation-exchange capacity (CEC) for the Fisher material

was 1.03 meq/100 g, as reported by White and Erickson (1980). Their determination was made by exchange with 1 M NH₄OH and analysis by atomic absorption of released cations.

Spot checks of several data points were made using a chemically untreated Cornish kaolin, RLO 2101, from English China Clays. The CEC was reported by the company to be 4 meq/100 g, and the surface area to be 9.8 m²/g. Mineral impurities were 3% mica only. Mica did not produce the reported luminescent phenomena.

The trace-element composition of the two kaolins was determined by X-ray fluorescence. Samples consisted of 2–4 mg of kaolin powder taped to a HAWP 0.45 μm Millipore filter with a 13-mm diameter. The samples were scanned with an energy-dispersive X-ray fluorescence (XRF) spectrometer. The hardware for the XRF spectrometer was supplied by the Ortec Corporation, and the necessary software and computer handling of data output were produced via a Data General Eclipse S/130 computer (64-k core, Tektronix graphics, and all necessary I/O devices).

The time of scanning was 10,000 sec. By using this data-collection time, the estimated minimum levels of detection (as found by using dilution techniques with

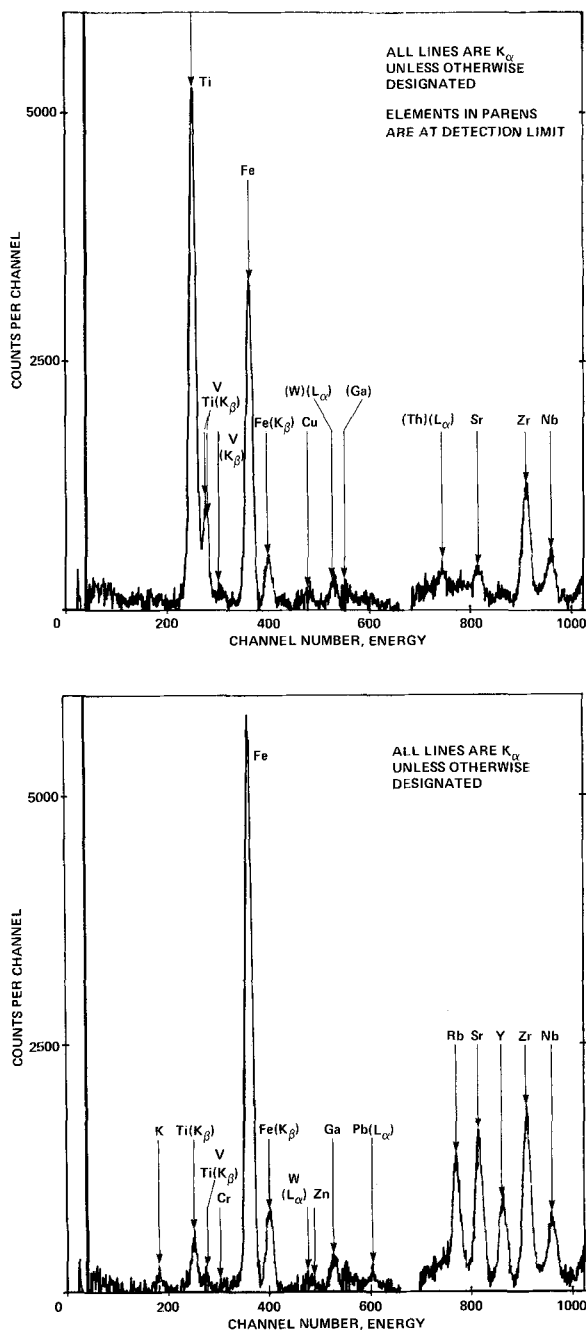


Figure 1. Trace element composition of Fisher (a) and RLO 2101 (b) kaolins as determined by X-ray fluorescence.

standard substances) was approximately 200 ng for elements in the atomic number range 23–50 and 5 μg for elements in the atomic number range of 50–94. Below atomic number 15 (phosphorous), the stimulated X-ray energy is too low to penetrate the Be window of the SiLi detector, and in the range of 15–20, detection limits increase from about 1 μg at $Z = 23$ to

perhaps 10 mg at $Z = 15$. The energy resolution of the SiLi detector was 172 eV at 519 keV. Background subtraction routines were computer-based using stored background spectra taken at the time the samples were run. Molybdenum ($Z = 42$) was used as an internal marker for channel identification and energy calibration.

The elemental composition of the Fisher samples (Figure 1b) was Ti, V, Fe, Cu, W (trace), Ga (trace), Th (trace), Sr, Zr, and Nb. The presence of Cu, Ga, Sr, Zr, and Ni was determined only by the energy of the $K\alpha$ line. W and Th were determined by $L\alpha$ lines. For Fe, Ti, and V, a $K\beta$ was also observed. The semi-quantitative estimations for Ti and Fe yielded 0.9% TiO_2 and 0.36% Fe_2O_3 .

The trace-element composition for sample RLO 2101 (Figure 1b) showed K (trace), Ti, V (trace), Cr (trace), Fe, W, Zn, Ga (trace), Pb (trace), Rb, Sr, Y, Zr, and Nb. With the exception of Ti and Fe, where both $K\alpha$ and $K\beta$ peaks were observed, and Pb and W, which were observed by the $L\alpha$ line, all elements were identified by means of the energy of the $K\alpha$ line. Semi-quantitative estimates for Fe and Ti in the sample RLO 2101 examined showed 0.49% Fe_2O_3 and 0.07% TiO_2 in moderately good agreement with the amounts 0.40 wt. % Fe_2O_3 and 0.18 wt. % TiO_2 reported by English China Clays. Agreement is within the accuracy of the X-ray fluorescence method employed. More quantitative measurements are in progress.

Cab-O-Sil grade M-5, a fumed Si of 0.014- μm particle size, surface area $200 \pm 25 \text{ m}^2/\text{g}$, as reported by the producer, Cabot Corporation, Boston, Massachusetts, was used without further treatment. Its water loss on heating for 3 hr at 300°C was $7.3\% \pm 0.1$. Neutral alumina, 400 mesh, with a water loss of $1.4\% \pm 0.1$ upon heating for 3 hr at 300°C, was used as received.

Organic amines

Amines were tested before and after purification. Purification of all amines, except hydrazine and pyridine, was accomplished by drying them over a heat-activated molecular sieve followed by distillation. Two samples of hydrazine were prepared: one (hydrazine A) from Eastman chemicals was distilled to bp 114–119°C and stored over a heat-activated molecular sieve; another (hydrazine B) from the same source, was dried over a molecular sieve and distilled from NaOH pellets at bp 114–115°C. Anhydrous hydrazine from Aldrich Company was used as received. Pyridine (pyridine A), Mallinckrodt Chemicals purified grade, which was dried over NaOH was compared with pyridine (pyridine B), Fisher, IR spectroanalyzed, similarly dried. The other amines were piperidine obtained from Matheson, Coleman and Bell, which was distilled and collected at bp 106.4°C; n-butylamine, obtained from Aldrich, which was distilled and collected at bp 78°C; monoethanolamine, obtained from Baker, which was distilled

Table 1. Visible-UV absorption data¹ for purified and unpurified amino compounds.

Organic amine	K_b	λ o.d. ² = 0.1 a.u. ³		λ o.d. ² = 1.0 a.u. ³	
		Undistilled A ⁴	Distilled B ⁴	Undistilled A ⁴	Distilled B ⁴
Piperidine	1.6×10^{-3}	4900	2915	4100	2880
n-Butylamine	4.1×10^{-4}	3000	2800	2600	2380
Monoethanolamine	2.8×10^{-5}	4600	2400	4100	2190
Hydrazine	3.0×10^{-6}	4400	3370	3280	3240
Pyridine	1.4×10^{-9}	—	4400	—	3400
Quinoline	6.3×10^{-10}	6200	4000	5000	3800

¹ Absorption data are from 1 cm of path of neat liquid and thus emphasize any long-wavelength contribution from possible contaminants. Reported literature values are for dilute solutions and are therefore inappropriate for comparison.

² o.d. = optical density.

³ a.u. = absorbance units.

⁴ See Experimental section for details of purification.

and collected at bp 170°C; and quinoline obtained from Aldrich, which was distilled and collected at bp 237.2°C. Improvement in purity was determined by observing the blue shift in the visible-UV spectra (using a Cary 14 spectrophotometer) of both the distilled and undistilled material. The values for the wavelength at which the absorbance reached optical densities of 0.1 and 1.0 are shown in Table 1 with the reported basicity constant, K_b , of the various amines (Lange, 1961).

Preparation of clay-amine mixtures for photon counting. Pyrex scintillation vials were boiled in concentrated nitric acid, thoroughly rinsed, and air dried. The clay was weighed directly into the scintillation vial. An appropriate weight of liquid was drawn into a glass pasteur pipet or a polypropylene dropper, weighed, and added directly to the clay. Typical compositions, by weight, of the sample pastes were 2:1 amine: kaolin, 1:1 amine: alumina, and 10:1 amine: Cab-O-Sil. An effort was made to apply a paste of greater than 100 μm thickness to minimize variation of the count rate resulting from differences in optical path traversed by the emitted light. At this thickness, the kaolin samples are totally absorbing (Coyne *et al.*, 1981a). The clay was spread upwards on the sides of the vial with a clean, stainless steel weighing spatula and vortexed, using a deluxe mixer from Scientific Products while rotating the vial in a nearly inverted position in order to even out non-uniformities of spreading. The vials were wiped with a damp towel immediately before insertion into the counter to diminish spurious count rates from electrostatic charges on the glass surface. These addition, smoothing, and cleaning operations were performed as quickly as possible, because maximal emission occurred in the first few seconds and was not captured by the counter. Some of the diminution of count rate with time is due to "sagging" of the film into the bottom of the flask. An accurate study of the kinetics of the decay process is clearly impractical under limits of the present experimental configuration, but the observed $\pm 15\%$ reproducibility is encouraging,

considering the crudeness of the present technique. Decay in the first minutes may be exponential, but over hours it is considerably slower. If a single process is responsible for all the emission of light, it must depend on some prior macroscopic changes in availability of the amino compound to the surface.

Preparation of gamma-irradiated samples. Samples to be gamma irradiated were weighed to the nearest 0.01 g on a Mettler Model S-5 single pan balance into borosilicate vials. The samples were then irradiated with gamma rays in the presence of air in a Gammacell 220 (Atomic Energy Co., Canada, Ltd.) Co⁶⁰ source. The dose rate at the time of irradiation was 1.02×10^{19} eV/g·hr (1.64×10^5 rad/hr) in Fricke dosimeter solution (Weiss, 1950). The dose rate in the clay was corrected for the electron density of the clay (3.0×10^{23} electron/g) compared to that of Fricke solution (3.3×10^{23} electron/g).

Photon counting. Luminescence measurements were made in a Packard Model 3320 Tri Carb scintillation counter with two EMI 9635QB phototubes out of coincidence, with discriminator settings of 50–1000 and full gain.

Optical filters. Transmission data for Pyrex (Corning No. 7740) and Vycor (Corning No. 7913) were provided by Ron Verkon of Corning Glass Works, Corning, New York. Transmission data for the Kodak 2a filter are available from Eastman Kodak Company, Rochester, New York 14650.

Spectroscopic analysis of hydrazine-induced emission. The wavelength dependence of the emission from kaolin/hydrazine mixtures was measured using a fluorometer from Spex Industries consisting of a Czerny-Turner monochromator blazed for maximum efficiency at 300 nm having a focal length of 0.22 m, f/4 aperture, and 3.6 nm/mm dispersion and using 5-mm slits, an RCA IP28 phototube operated at 850 V, and a Spex Datamate microprocessed spectrometer-con-

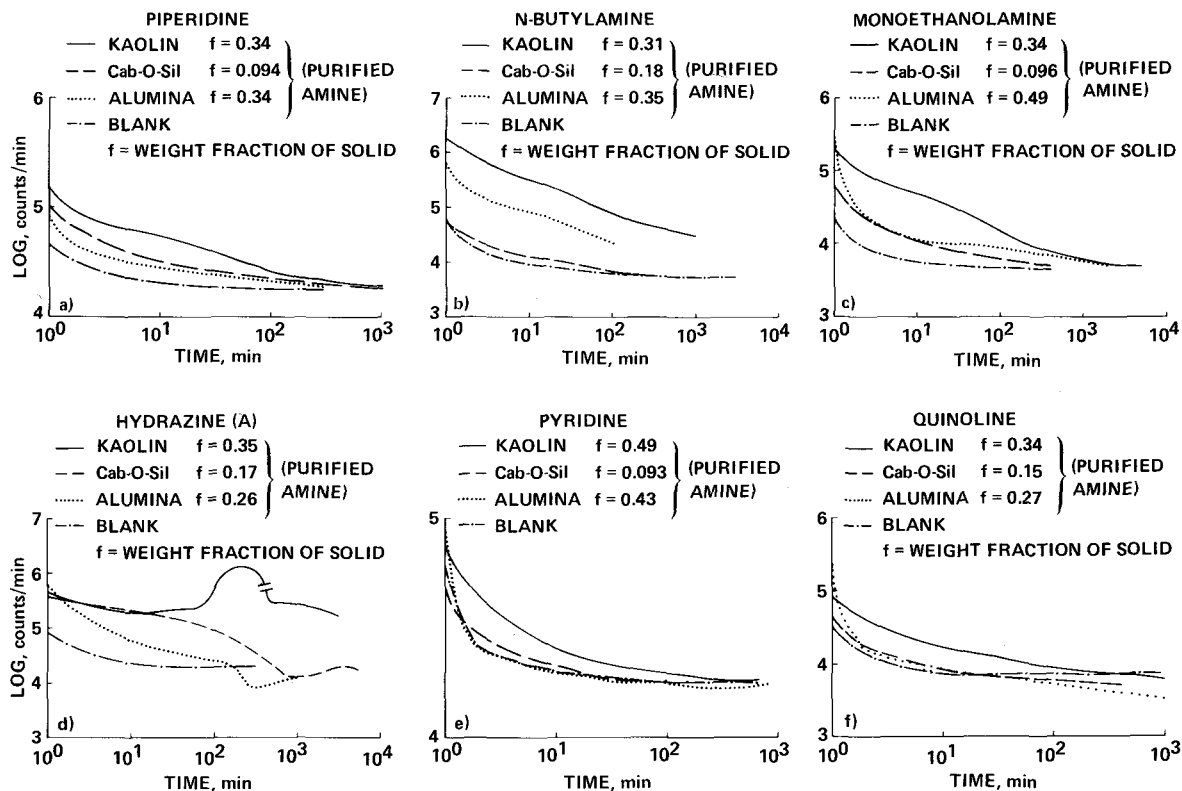


Figure 2. Photon output induced in kaolin, alumina, and Cab-O-Sil by (a) piperidine, (b) n-butylamine, (c) monoethanolamine, (d) hydrazine (A) (the kaolin and hydrazine has a time gap of unknown length), (e) pyridine, and (f) quinoline.

troller and data-acquisition processor. The number of scans was 50 for the three Cornish kaolins. The photocurrent was monitored at 1 nm intervals from 200 to 550 nm with a 0.5-sec dwell time on each channel.

RESULTS

Photons were released when kaolin or its constituents—silica or alumina—were mixed with each of the organic amines tested. The overall photon yield and the time-dependence of the release were dependent on both the amine structure, its basicity, purity, and dryness, and the composition of the solid substrate, and on its state of pretreatment by preheating or pre-irradiation.

The pattern of photon release produced by the six compounds tested is shown in Figure 2. Photon release from alumina was initially higher than from the other solids but decayed much more rapidly to the background count rate of the solvent blank. The rate of photon release from Cab-O-Sil and kaolin decreased slowly, with a time scale for return to the background solvent count rate of hours instead of minutes. The total photon output from Cab-O-Sil and alumina generally was significantly less than that from kaolin. The kinetics of photon release did not follow any simple

law, but given the present experimental arrangement, several variables which might have been expected to affect the kinetics cannot be rigorously controlled. The count rate in the first few seconds of the interaction between substrate and amine could not be monitored. Optical similarity between the various solid substrates, optical uniformity over the entirety of the emitting surface and optical constancy of the film over the extended time of the measurements cannot be guaranteed. Reproducibility of the curves shown was within 10–15% for amines of comparable purity and dryness. A number of small errors resulted from drift in the dark current over the extended periods involved in the counting, sag of the film, and, perhaps, changes in the purity or dryness of the amine. This problem was minimized by examining two solids at once on different counters and by changing the order of the solids to be run immediately after a distillation. Backgrounds shown should be viewed as approximate, rather than absolute, as the different counts had slightly different characteristic dark count rates, and the blank was usually measured soon after distillation of the amine in order to avoid overestimating the difference between blank and solid. The data shown were selected to avoid biases and represent replicable effects; however, considerable

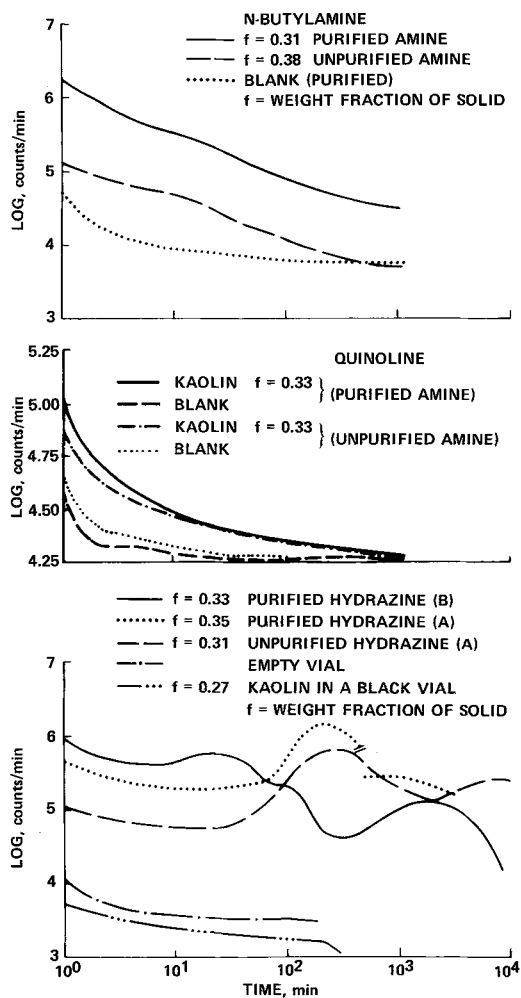


Figure 3. Photon output induced in kaolin by purified and unpurified amines: (a) hydrazine (A, B) (the sample with purified hydrazine has a time gap of unknown length), (b) n-butylamine, and (c) quinoline.

development of methods and instrumentation will be required to produce quantitatively reliable count rates and kinetics.

Sample count rates were higher from higher-purity, drier solvents (Figure 3), probably because diminished self-absorption is to be anticipated by purer, less-colored solvents. The background count rate produced by interaction between the amine and the vial, however, was higher for unpurified solvents (e.g., Figure 3b).

The emission from hydrazine was particularly sensitive to the purity and dryness of the hydrazine. Qualitatively, the results from the two batches of hydrazine were similar in their high count rates and in the delayed rise in count rate, but the details of the time scale and magnitude of the delayed rise were significantly different. An appreciable amount of this difference may have been due to the fact that hydrazine A contained a sig-

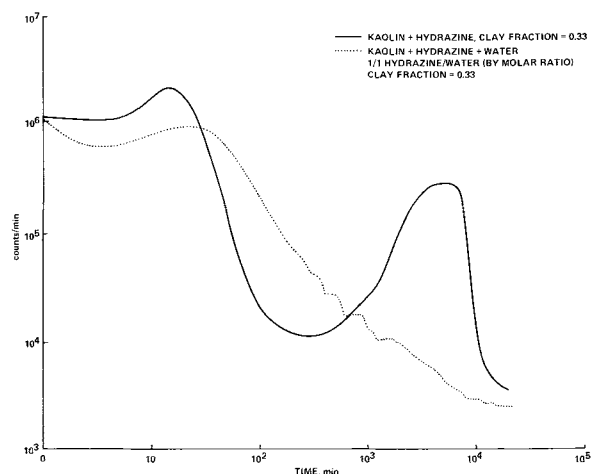


Figure 4. Photon output induced in kaolin by Aldrich hydrazine and Aldrich hydrazine plus equimolar water.

nificant fraction of hydrazine hydrate (bp 118°–119°C). To test this hypothesis, equimolar amounts of water were added to the higher purity, drier hydrazine. The results are shown in Figure 4. Intercalation by hydrazine of the Fisher kaolin was complete in 45 min as determined by X-ray powder diffraction. Long-range studies are being undertaken in this laboratory to associate the luminescence more quantitatively with both the degree of wetness and the degree of intercalation of kaolin by hydrazine. Extensive light production by the interaction of kaolin and hydrazine was characteristic of all tested kaolins, but the prominence, number (1 or 2), and duration of the delayed peaks were somewhat variable.

The effects of preheating (hydrazine B) and pre- γ -irradiation (hydrazine A) on light output are shown in Figures 5 and 6. The light output, as a function of preheating temperature, fell into three crude temperature ranges: (1) Ambient $\leq T \leq 250^\circ\text{C}$ in which preheating caused some enhancement of the monotonically decaying portion, (2) $300^\circ\text{C} \leq T \leq 400^\circ\text{C}$ in which the monotonically decaying component was enhanced, and the delayed peak was further delayed and diminished but could be partially or completely restored by irradiation, and (3) $400^\circ\text{C} \leq T \leq 900^\circ\text{C}$ in which both the delayed peak and the monotonically decaying portion of the photon count were seriously diminished or destroyed. The temperature data were less reproducible than the other effects shown because both amine dryness and time between clay heating and application of amine have strong quantitative effects. The qualitative trends, however, are reliably reproducible. The temperature dependence of amine-induced light output has been checked only for hydrazine. Also the temperature ranges where hydrazine-induced luminescence changes in intensity have been checked only for one kaolin. The

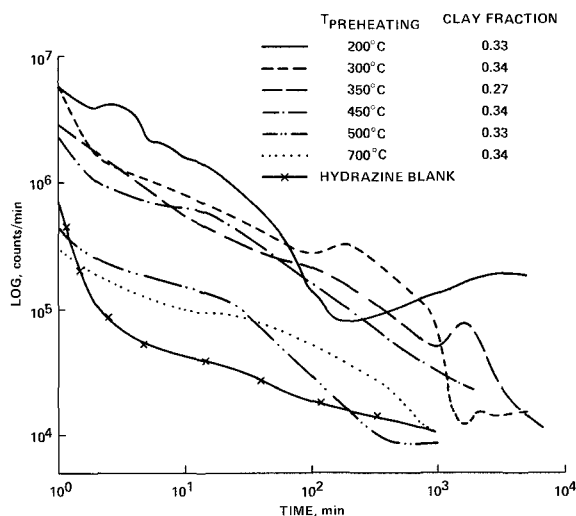


Figure 5. Photon output induced in preheated kaolins by hydrazine (B).

generality of the observed changes to varied kaolins, the associations of luminescence with subtle structural variations or impurity levels of the kaolin and the structure and purity of the organic liquid is, as of yet, incomplete. The amount of light produced by different kaolins upon interaction with hydrazine, however, varied between kaolins in crude proportion to the light produced upon dehydration. For instance, upon dehydration a sample of RLO 2101 Cornish kaolin from English China Clays produced roughly 100 times as much light as did the Fisher kaolin used for most of the reported studies. At least that much more light is produced upon interaction with hydrazine.

The wavelength distribution of the light released by hydrazine was qualitatively assessed from the following: (1) The response of the EMI 9635 QB tube was maximal in the near-ultraviolet at 3700 Å, dropping off only slowly into the ultraviolet but rapidly toward the red end of the spectrum. (2) Tests of the initial photons released from mixtures of hydrazine and kaolin indicated a substantial increase in the photon yield when Vycor 7913 was substituted for Pyrex containers. Vycor is more transparent than Pyrex in the near-ultraviolet. The effect of the composition of the containing vial on the photon output and the wavelength dependence of the light yield is being examined more closely. (3) Insertion of a Kodak 2a filter with an o.d. >2, cut off at 410 nm, substantially diminished the light output. (4) The energy during the light-emission peak induced by hydrazine of the three Cornish kaolins is 3.4 eV (365 nm) (Figure 7). Thus, the photons observed were in the blue to near-ultraviolet region of the spectrum.

A delayed burst of photons was also produced when low-boiling amines, n-butylamine, and piperidine were

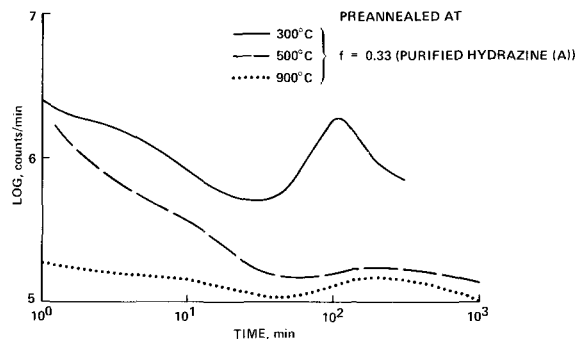


Figure 6. Photon output induced in preannealed, γ -irradiated kaolin by hydrazine (A).

removed, using an inner chamber of H_2SO_4 (e.g., Figure 8). This effect was clearly discernible only with the highly luminescent Cornish kaolin.

DISCUSSION

The interaction of amines with clay surfaces is a complex process which has been extensively, but not exhaustively, investigated (see reviews by Theng, 1974; van Olphen, 1977). Several types of water are known: superficially adsorbed water (it is this type which is apparently associated with the dehydration-induced luminescence); hydration water of the exchangeable cations; and water hydrogen-bonded directly with the clay surface. In addition, the amines themselves can complex with the clay surfaces (see Theng, 1974, 84–110.)

The ability of an amino compound to replace exchangeable cations in montmorillonites has been related to various molecular parameters, including K_b (Theng, 1974, 108). No clearcut relationship appears to exist between the photon yield and K_b in the series of amines reported here or in some others, not shown; however, the amines chosen for this experiment have variable UV absorption spectra and were selected to maximize the variability of K_b , rather than for structural analogy. It is possible that correlation between photon output and K_b might be discerned in studies of several homologous series of amino compounds.

The photon yield from hydrazine observed in this study is unique in two respects: not only is the overall photon output considerably higher than that of the other amines, but also one or two photon bursts were observed that were delayed from the time of mixing and initial monotonic decay. Because a burst of photons delayed from the introduction of desiccant was observed upon removal of water and some amines with low boiling points from kaolin, it is tempting to associate these effects. For this reason, the dependence on preheating and pre- γ -irradiation of the delayed burst produced by hydrazine was investigated. These treatments had profound effects on the dehydration-in-

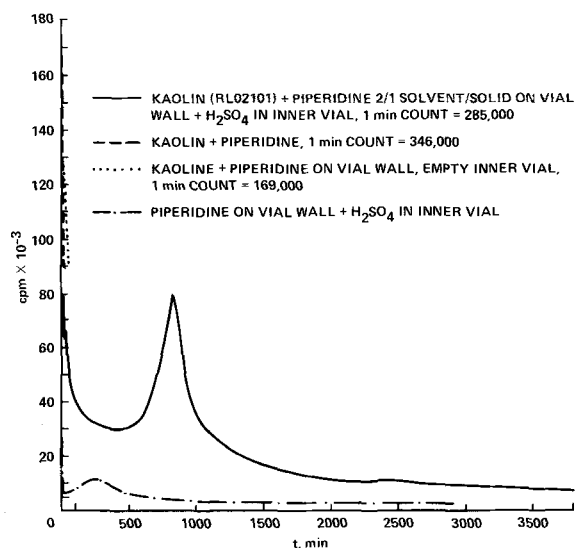


Figure 7. Photon output induced upon removal of piperidine by take-up into sulfuric acid.

duced luminescence (Coyne *et al.*, 1981b; Coyne and Sweeney, manuscript submitted for publication).

Monotonically decaying count rates induced by hydrazine were increased by moderate preheating and by pre- γ -irradiation. In contrast, the monotonically decaying portion of the dehydration-induced luminescence curve was relatively insensitive to preheating. It was very sensitive to recent γ -irradiation, but the sensitivity decreased rapidly with the interval between irradiation and measurement. For both water removal and hydrazine addition there appeared to be critical temperatures above which no delayed luminescence peak was produced after preheating, and no restoration of the capacity to produce the delayed peak after it has been destroyed by preheating could be produced by γ -irradiation, after heating, but before measurement. The critical temperature ranges for dehydration-induced luminescence were 250°–300°C for destruction reversible by γ -irradiation and 350°–400°C for irreversible destruction of the delayed peak in the Fisher kaolin. Insufficient data exist to define these temperature ranges for the preheating induced reversible and irreversible destruction of the delayed luminescence induced by hydrazine, if indeed they are as clearly defined as for the dehydration-induced effect, but preliminary data indicate that they do exist, albeit at somewhat higher temperatures than for the dehydration-induced effect. Inasmuch as the overall count rate is higher from hydrazine/kaolin mixtures, this apparent increase in the temperature range required to destroy the hydrazine-induced delayed peak may be an artifact of increased signal to noise ratio from the sample of higher count rate. There is no delayed burst from blanks or oxides, further associating the burst with the struc-

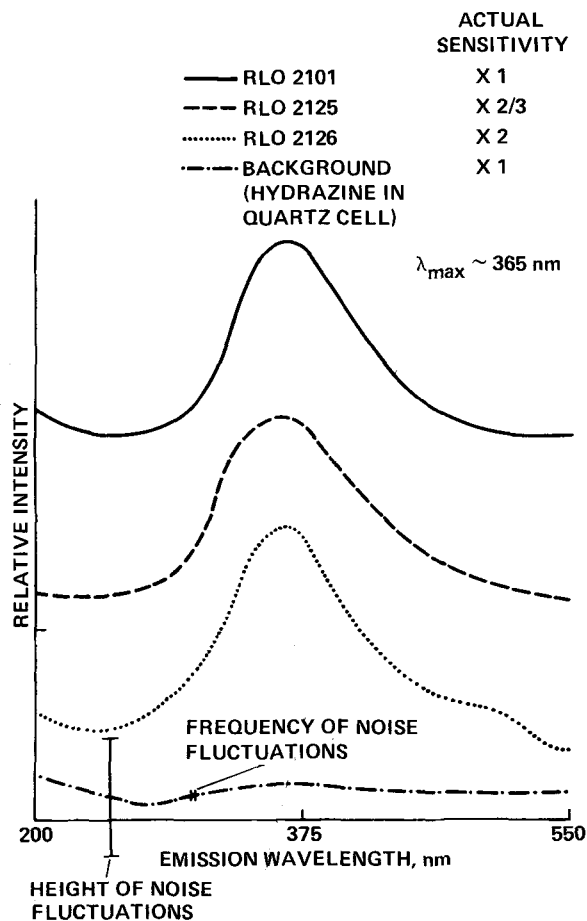


Figure 8. Wavelength dependence of desolvation luminescence of Cornish kaolins induced by hydrazine.

ture of kaolin or a ubiquitous kaolin impurity and also eliminating chemiluminescent decomposition of hydrazine, as an artifact, unless this reaction was uniquely catalyzed by kaolin or its characteristic impurities. The possibility of hydrazine decomposition accompanying light release is under investigation.

Interesting though the parallels may be between photon output from hydrazine/kaolin and water/kaolin mixtures, the differences are perhaps more significant. The hydrazine effect arises after introduction of liquid, the dehydration effect upon removal of liquid. Whether desolvation of hydrazine-saturated kaolin produces another delayed burst analogous to that from *n*-butylamine and piperidine has not been investigated. The hydrazine effect is more prolonged than the dehydration-induced effect.

The delayed bursts were confined to hydrazine among the amines tested. In this regard it is interesting to note that hydrazine intercalates the tightly hydrogen-bonded layers of kaolin (e.g., Ledoux and White, 1966). It is possible that the earlier delayed burst arose from a

different mechanism than that producing the later prolonged burst, perhaps the intercalation itself, but it is not yet possible to discriminate between several possible mechanisms for the light production. Among the more plausible ones are the following:

(1) Photons are released when occluded water or exchangeable cations are expelled after penetration of the amine into wedges produced by partial weathering.

(2) If internally charge-compensated, cation-substitution sites exist in kaolin, photons may be released when residual hydration water of exchangeable cations associated with those sites is made accessible by intercalating hydrazine molecules.

(3) Photons are released as a consequence of mechanical stress produced during the intercalation process.

(4) Photons are the product of a chemiluminescent surface reaction following slow buildup of a precursive reactant. The reaction might be between hydrazine and clay, included mineral impurity, or adsorbed organic impurity. An impurity common in kaolins and capable of catalyzing hydrazine decomposition is iron.

(5) Photons may be released by the recombination of either trapped, separated charges or liquid/surface interfacial charges moving under an interfacial potential gradient. This gradient would extend throughout the space charge region produced by the interface-induced bending of the kaolinite electronic band structure analogous to that in other materials (Bard, 1980). Reversible band bending upon change of interface from gas liquid and vice versa may explain the fact that both solvation and desolvation emission is observed; however, the long duration of the solvation-induced luminescence is difficult to explain by this mechanism. Efforts are in progress to discriminate among these possibilities.

The molecular origin of the delayed luminescence produced by hydrazine is yet unassigned. The frequency dependence for the emission (Figure 7) may or may not be similar to that for dehydration-induced luminescence. That it is produced by some charge redistribution in the bulk clay mineral and not by a surface-adsorbed impurity is supported by a strong dependence of the effect on preheating pre- γ -irradiation, clay purity, and crystallinity, which is analogous to the similar dependency of dehydration-induced luminescence also observed in this laboratory.

That the hydrazine-induced luminescence intensity characteristic of a given kaolin changes proportionally to the change in the dehydration-induced luminescence intensity when a different kaolin is used, supports the possibility that the two effects are associated with some electronic event in common with both kaolins. Whether the common event is a common luminescent center with different concentrations in the two materials, or whether the concentration of the luminescent center is similar in the two materials and the electronic pro-

cesses preceding the luminescent event occurs to a different degree in different materials, has yet to be determined. At present, no single hypothesis seems adequate to explain all of the observed data. In particular, the possible role of iron is of interest, but offers no clearcut interpretation. Both dehydration-induced and hydrazine-induced luminescence from the Fisher kaolin are less by nearly a factor of 100 than that from the RLO 2101 kaolin, but the iron content of these materials as measured by XRF is similar within a factor of two. Also, it is chemically plausible that iron might be instrumental in the hydrazine effect, as Fe_2O_3 will catalytically decompose hydrazine. It is more difficult, however, to postulate a role for iron in dehydration-induced luminescence, particularly because Fe_2O_3 alone does not produce dehydration-induced luminescence and iron generally serves as a quencher of luminescent processes in solids. It was for these sorts of reasons that the trace element composition of the kaolins was measured, as trace metal ions frequently serve as activators or quenchers of luminescent phenomena in minerals, or even as the originators of the luminescence itself. No firm conclusions can be drawn here because information is required not only about the existence of trace contaminants, but about their location and molecular environment relative to the luminescing centers and the degree to which they are essential to the luminescent process.

CONCLUSIONS

The foregoing data associating light emission with interaction of kaolin and organic amines are of interest in studies of the structure/reactivity relationships of clay minerals. Because light emission is indicative of either the production and/or relaxation of excited states, photon release upon solvation and desolvation of kaolin indicates that electronically excited states of kaolin are: (1) measurably populated without external irradiation, and (2) produced, quenched, or redistributed by heating in the temperature range $100^\circ \leq T \leq 450^\circ\text{C}$. That luminescent phenomena in kaolin are produced by solvation/desolvation interactions, mechanical stress, or intercalation suggests that electronically excited states may be involved in the chemical reactivity of the material or useful in monitoring chemical and physical changes in the material.

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Резюме—Наблюдалось несколько новых, люминесцентных явлений при окружающей температуре, происходящих из взаимодействия каолина с разными аминными соединениями. Показано, что эмиссия света из каолиновых паст (обработанных квинолином, пиридином, гидразином, моноэтанолламином, n-бутиламином и пиперидином) исчезала монотонически в течение от нескольких часов до нескольких дней. Большое количество света выделялось данным аминным соединением после осушки и очистки. Гидразин, дополнительно к монотонически исчезаемому выделению фотонов, создает замедленные импульсы света с максимальной эмиссией при длине волны 365 нм. Эти импульсы сохраняются от нескольких часов до нескольких дней и являются чувствительными к начальной степени сухости гидразина как по количеству импульсов, так и по интегрированному выходу фотонов. Количество света и способность каолина производить замедленные импульсы являются сильно зависимыми от предварительного нагрева и от гамма-облучения аналогично импульсом света, вызванным дегидратацией, как это было предложено ранее в Амесском Исследовательском Центре. Малый замедленный взрыв фотонов происходил, когда пиперидин и n-бутиламин удалялись путем выпаривания в резервуар H₂SO₄. [E.G.]

Resümee—Es wurden einige neue Phänomene bei der Raumtemperatur-Lumineszenz beobachtet, die ihre Ursache in der Wechselwirkung von Kaolin mit verschiedenen Amino-Verbindungen haben. Es wurde gezeigt, daß die Lichtemission von Kaolinpasten (behandelt mit Quinolin, Pyridin, Hydrazin, Monoäthanolamin, n-Butylamin, und Piperidin) gleichmäßig über einen Zeitraum von Stunden bis Tagen abnimmt. Mehr Licht wurde von einer gegebenen Aminoverbindung ausgesendet, nachdem sie getrocknet und gereinigt wurde. Hydrazin liefert—zusätzlich zu der allmählich abnehmenden Photonen-Aussendung—verzögerte Lichtpulse, die einige Stunden und einige Tage andauern, und deren Wellenlänge am Emissionsmaximum 365 nm beträgt. Diese Photonenaussendungen hängen ganz eng von der ursprünglichen Trockenheit des Hydrazin ab, sowohl was die Anzahl der Aussendungen und die integrierte Photonenausbeute betrifft. Die Lichtmenge und die Fähigkeit des Kaolin, verzögerte Aussendungen zu liefern, scheint sehr stark von der vorhergehenden Wärmebehandlung und Gammabestrahlung abzuhängen, entsprechend den durch Dehydratation verursachten Lichtpulsen, die kürzlich vom Ames Research Center berichtet wurden. Eine kleine verzögerte Photonenaussendung tritt auf, wenn Piperidin und n-Butylamin durch Verdampfung in ein H₂SO₄-Reservoir entfernt wurden. [U.W.]

Résumé—Plusieurs nouveaux phénomènes luminescents à température ambiante, résultant de l'interaction du kaolin et de composés aminés variés ont été observés. On a montré que l'émission de lumière de pâtes de kaolin (traitées avec de la quinine, de la pyridine, de l'hydrazine, de la monoéthanolamine, de la butylamine-n, et de la pipéridine) a diminué monotoniquement sur une période de plusieurs heures à plusieurs jours. Un composé aminé donné a émis d'avantage de lumière après avoir été séché et purifié. En plus de l'émission de photons diminuant monotoniquement, l'hydrazine produit des poussées de lumière retardées avec des longueurs d'onde d'émission maximales de 365 nm qui ont duré de plusieurs heures à plusieurs jours. Ces éclats de photons sont très sensibles à la sécheresse initiale de l'hydrazine, à la fois en ce qui concerne le nombre d'éclats et la production intégrée de photons. La quantité de lumière et la capacité du kaolin pour produire l'éclat retardé semblaient fortement dépendre de l'échauffement préliminaire et de l'irradiation-gamma, de manière analogue à la poussée de lumière induite par la déshydratation rapportée précédemment par l'Ames Research Center. Un petit éclat retardé de photons s'est produit lorsque la pipéridine et la butylamine-n ont été enlevées par évaporation dans un réservoir H₂SO₄. [D.J.]